THERMOCHEMICAL STUDY OF CRYSTALLINE SOLUTES DISSOLVED IN TERNARY HYDROGEN-BONDING SOLVENT MIXTURES

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Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

May 2001

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Pribyla, Karen J., Thermochemical Study of Crystalline Solutes Dissolved in Ternary Hydrogen-Bonding Solvent Mixtures. Doctor of Philosophy (Chemistry), May 2001, 236 pp., 55 tables, 257 references.

The purpose of this dissertation is to investigate the thermochemical properties of nonelectrolyte solutes dissolved in ternary solvent mixtures, and to develop mathematical expressions for predicting and describing behavior in the solvent mixtures. Forty-five ternary solvent systems were studied containing an ether (Methyl *tert*-butyl ether, Dibutyl ether, or 1,4-Dioxane), an alcohol (1-Propanol, 2-Propanol, 1-Butanol, 2-Butanol, or 2-Methyl-1-propanol), and an alkane (Cyclohexane, Heptane, or 2,2,4-Trimethylpentane) cosolvents. The Combined NIBS(Nearly Ideal Binary Solvent)/Redlich–Kister equation was used to assess the experimental data. The average percent deviation between predicted and observed values was less than ± 2 per cent error, documenting that this model provides a fairly accurate description of the observed solubility behavior. In addition, Mobile Order theory, the Kretschmer–Wiebe model, and the Mecke–Kempter model were extended to ternary solvent mixtures containing an alcohol (or an alkoxyalcohol) and alkane cosolvents. Expressions derived from Mobile Order theory predicted the experimental mole fraction solubility of anthracene in ternary alcohol + alkane + alkane mixtures to within ± 5.8%, in ternary alcohol + alcohol + alkane mixtures to within ± 4.0%, and in ternary alcohol + alcohol + alcohol mixtures to within ± 3.6%. In comparison, expressions derived from the Kretschmer–Wiebe model and the Mecke–Kempter model predicted the anthracene solubility in ternary alcohol + alkane +

alkane mixtures to within ± 8.2% and ± 8.8%, respectively. The Kretschmer–Wiebe model and the Mecke–Kempter model could not be extended easily to systems containing two or more alcohol cosolvents.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER ONE

INTRODUCTION

Saturation solubilities for many compounds in a single solvent are published in tabulated form. In recent years, researchers have begun to measure and publish solubility data for solutes dissolved in binary solvent mixtures. Data for ternary systems are scarce, and data for higher order multicomponent systems are virtually nonexistent. With the importance of solubility information and the increased time involved in measuring thermodynamic properties for each additional component beyond binary systems, it is necessary to develop predictive methods to generate the desired properties in a solvent system from pure component physical properties, measured binary data, and/or structural information.

Over the past one hundred fifty years, several theories for predicting solubility have been developed. The early theories assumed ideal solutions, but nonelectrolyte solutions are rarely ideal. The introduction of the concept of activity coefficients into Raoult's partial pressure expressions allowed thermodynamic treatment of nonelectrolyte solutions. Flory and Huggins based their model on the concept of a crystalline lattice as a model for the liquid state, but a semi-empirical term based on volume fractions was included in the expression for the enthalpy of mixing. Huyskens and Haulait-Pirson developed an expression for the entropy of mixing. The latter expression is an arithmetic average of the Raoult's Law expression and the Flory-Huggins configurational model.

The Scatchard-Hildebrand solubility parameter model addressed solute solubility in systems containing only nonspecific interactions with the introduction of solubility parameters. For mixed solvents obeying a general mixing equation in which only nonspecific interactions are important, the Nearly Ideal Binary Solvent (NIBS) Model also has been successful in predicting solubilities through introducing weighting factors. These factors try to take into account the probability of interactions between any given two molecules in solution. The Wilson Model considered solutions where the components differ in molecular size and intermolecular forces by introducing parameters defined in terms of molar volumes and pair potential/interaction energies between like and unlike molecules.

A more recent model, defined by Mobile Order Theory, not only takes into account nonspecific interactions between solvent molecules, but also factors in the chemical reaction of hydrogen bonding between solvent molecules. Mobile Order Theory predicts solubility based on the fractions of time that a hydroxylic proton is either free or involved in hydrogen-bond formation. The thermodynamic expressions derived from using the Mobile Order Theory do not involve stoichiometric considerations of the actual complexes formed.

Previous coworkers in the Acree[1-5] group showed that the Mobile Order Theory gives reasonable predictions for the solubility of a crystalline solute in binary alkane + alcohol, alcohol + alcohol, alcohol + alkoxyalcohol, and alkoxyalcohol + alkoxyalcohol solvent mixtures. It is the purpose of this dissertation to show that the Mobile Order Theory can be extended to predict the solubility of a crystalline solute in ternary systems,

such as alkane + alkane + alcohol, alkane + alcohol + alcohol, alkane + alkane + alkoxyalcohol, and alkane + alcohol + alkoxyalcohol. Previous students in the Acree research group (Zvaigzne, Powell, and McHale) have examined the ability of Mobile Order theory to predict the solubility behavior of anthracene and pyrene in the various sub-binary combinations of alkane, alcohol and alkoxyalcohol solvents. While these earlier studies did show that the predictive applicability of Mobile Order theory was comparable to the more traditional, conventional solution models currently used in the chemical industry, there still remained several unanswered questions regarding: (1) how easy it would be to extend the basic model to higher-order systems; (2) how easy it would be to introduce solute-solvent complexation into the model; (3) whether the model could be used for more soluble solutes where infinite dilution approximations did not apply; and (4) whether the model would continue to provide very good predictions in solvent systems that covered much larger ranges in saturation mole fraction solubilities.

From a predictive standpoint it is very easy to predict the solubility of a solute in a system that covers a very small mole fraction range. For example, in the case of anthracene dissolved in an equimolar mixture of cyclohexane and heptane one would expect the measured mole fraction solubility to fall somewhere between anthracene's measured mole fraction solubility in pure cyclohexane (χ_A^{sat} = 0.001 553) and in pure heptane (χ_A^{sat} = 0.001 571). As indicated by the experimental values within the parentheses, anthracene has virtually the same solubility in both hydrocarbon solvents. It would be much more difficult for one to predict anthracene's solubility in an equimolar mixture of 2-propanol (χ_A^{sat} = 0.000 411) and 1,4-dioxane (χ_A^{sat} = 0.008 329). Now the

mole fraction solubility range is much larger. Anthracene is twenty times more soluble in 1,4-dioxane than in 2-propanol. Experimental anthracene solubility data is available in the chemical literature[1-5] for several ternary solvent systems. The literature data was never explained in terms of Mobile Order theory or in terms of the two major competing association models (the Kretschmer–Wiebe model and the Mecke–Kempter model). The anthracene solubility data that is available in the chemical literature covers only a four-fold range in mole fraction solubility. The solubility of anthracene in ternary alkane + alcohol + ether solvent mixtures was measured as part of this dissertation research[6-14] in order to have data that cover a much larger 20-fold range in mole fraction.

To set the stage for understanding the importance of the research presented in this dissertation, we need to introduce the term partition coefficient. The partition coefficient is the ratio of the concentration of a given substance in the organic phase, compared to the concentration of the same substance in the aqueous phase, after the two immiscible phases are mixed and then allowed to equilibrate. For example, when an aqueous solution of iodine is shaken with an immiscible organic solvent, such as hexane, a portion of the iodine is extracted into the organic layer. The equilibrium established between the two phases can be described by

$$I_{2(aq)} \rightleftharpoons I_{2(org)}$$

The equilibrium constant, K_d, for this "reaction"

$$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$$

is called a distribution or partition coefficient.[15] Numerous studies have shown that partition coefficients can be approximated as the ratio of the solute's solubility in two phases.[16] There are many areas where the partition coefficient (thus, the solubility) controls the equilibrium process in a particular system.

One might say that life itself depends on partition coefficients. Partitioning allows the nutrients from the food we eat to end up in our cells. Partitioning allows the oxygen we breathe into our lungs to supply the oxygen the cells need. The pharmaceutical industry is aware of the partitioning processes that occur in the human body. Medications given in liquid dosage forms must be formulated to dissolve in the blood stream (a primarily aqueous system) for circulation throughout the body, and then partitioned into the cells to be used in biochemical process (organic systems). Similarly, medications given in "time capsule" form must either dissolve or partition from (or through) a semi-porous pharmaceutical formulation in a well-controlled time manner before the drug molecule can be delivered to its target site.

Organisms may accumulate chemical substances either directly from the surrounding environment or from their diet. Nondietary bioaccumulation in aquatic organisms is referred to as bioconcentration and may be viewed as a process in which the substance is distributed between the organism and the environment in accordance with the substance's chemical properties, environmental conditions, and biological factors, such as the organism's ability to metabolize the substance. The tendency of a waterborne substance to bioconcentrate in aquatic organisms is usually expressed as its

bioconcentration factor (BCF), which is formally defined as the equilibrium ratio of the concentration of the substance in the exposed organism to the concentration of the dissolved substance in the surrounding environment. The BCF is an important parameter in environmental assessment. Bioconcentration emerged as an ecological concern more than forty years ago when studies demonstrated that the accumulation of pesticide residues in fish led to reproductive failure in some birds. Humans are also consumers of fish and shellfish, and exposure assessments now routinely consider fish ingestion as a potential route of human exposure to chemicals in the environment. The assumption is that bioconcentration is a thermodynamically driven partitioning process between water and the lipid phase of the exposed organism.[17]

For many years, exhaust emissions from gasoline and diesel powered vehicles have been studied primarily because of their adverse health effects. In comparison to gasoline engines, diesel engines are known to have better fuel efficiency and emit smaller amounts of volatile organic carbon and CO_2. However, they are also known to create much larger amounts of particulate matter, as well as many polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons consist of two or more fused aromatic rings. Some PAHs are known to be powerful carcinogens to humans.[18] The extent of human exposure to the PAHs depends on partitioning between gas and particle phases, as well as the size distribution of the particulate fraction containing the PAHs. There is a much greater potential carcinogenic effect if the PAHs are components of particles that penetrate and deposit into the bronchioles and alveoli of the lungs.[19]

PCBs and other semivolatile persistent, bioaccumulatory organic contaminants reach human tissue primarily via dietary intake, through the ingestion of meat, dairy products, and fish generally dominating dietary exposure to PCBs for the average consumer. Grazing animals, therefore, supply PCBs to humans from the terrestrial environment. They, in turn, receive PCBs primarily through the ingestion of grass, silage, and concentrate feed. PCBs and similar compounds reach grass and other vegetation principally via atmospheric deposition. There is a clear link along the pathway air-vegetation-grazing animals-meat/dairy products, which results in human exposure to PCBs and a range of other persistent organic pollutants. As a consequence of atmospheric emissions which affect air concentrations, persistent organic pollutants will ultimately exert a strong influence on human tissue concentrations. Given the importance of the air-grazing animal pathway, researchers have been studying the range of processes which "control" the partitioning kinetics of persistent organic pollutants transfer between air-vegetation and grazing animal feed-milk/body fat.[19,20]

There is evidence that the atmospheric gas/particle partitioning of polynuclear aromatic hydrocarbons (PAHs) and other semivolatile organic compounds (SOCs) is primarily absorptive in nature and can be described by gas-liquid interaction processes under many conditions. Ambient humidity can directly influence the partitioning on different types of particles. Experimental results show that the partitioning of semivolatile organic compounds to "dry" particles is higher than that to "wet" particles. For less polar aerosols, such as diesel soot particles, the effect of humidity on partitioning of SOCs is not as important.[21]

Absorption of contaminants from aqueous solutions into the natural organic matter, or mineral components of sediments or soils, is related to partitioning.[22] Because the PAHs in soils are strongly associated with the organic matter fraction, the PAHs are not expected to be susceptible to plant uptake. If that is indeed the case, then the main pathway for PAHs to accumulate in above ground plant tissues must be from the air to leaf surface. However, the partition of these lipophilic compounds from the outer leaf to the inner would require transport by the phloem which is also water based, and this rarely happens. Even so, particle-bound PAHs have been found in vegetation, and gas-phase deposition has been suggested as the predominant pathway. There is currently considerable interest in studying the uptake of organic chemicals by plants. Models have been developed which use the physico-chemical properties of compounds as input data. One of the essential physico-chemical properties needed for these studies is solubility.[23]

With the present trend in the petroleum industry toward heavier feedstocks rich in PAHs and coal-derived liquids, there is a strong need for expansion of the database of thermodynamic data on heavier compounds than presently exists. For design purposes, activity coefficient data, as well as solubility data, will be important in that the precipitation of these heavy components will plug lines and vessels. The necessary activity coefficient data can be calculated from solid-liquid solubility data.[24]

Many analytical methods involve chemical separations and/or solute partitioning between two immiscible phases. All separation processes have the distribution of the components in a mixture between two phases that subsequently can be separated

mechanically in common. Separations by precipitation require large solubility differences. If the ratio of the amount of one particular component in each phase (the distribution ratio) differs significantly from that of another, a separation of the two is potentially feasible.

Extraction procedures are based upon distribution equilibria between immiscible solvents. A very high distribution coefficient might require only a few extractions to remove a contaminant. If the distribution coefficient is not favorable, hundreds of automatic successive extractions may have to be performed to complete the removal of a contaminant. Examples of extraction procedures include the removal of metal ions as chelates. A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a 5- or 6- membered heterocyclic ring. [15] Metal chelates are relatively nonpolar, uncharged complexes, and have solubilities low in water, but high in organic liquids. Many chelating agents are weak acids. Distribution ratios for such reagents vary widely among cations and can be controlled by changes in pH and reagent concentration, thus making many useful extractions possible. Controlled pH can be used to extract iron from steel or iron ore samples prior to analysis for such trace elements as chromium, aluminum, titanium, and nickel. Certain nitrate salts, such as uranium (VI) can be extracted from lead and thorium by ether extraction.

All chromatographic separations are based upon differences to the extent in which solutes are partitioned or distributed between the mobile and the stationary phase. In gas-liquid chromatography (GLC), the stationary phase is a liquid that is immobilized on the surface of a solid support by adsorption or chemical bonding. The rate of movement of

an analyte through the column is determined by its distribution ratio between the gaseous phase and the immobilized liquid phase.[25] GLC can be used to perform separations and analyses, although its uses for qualitative purposes are very limited. An example of this type of analysis is that of identifying the source of an oil spill. By comparing petroleum biomarkers from the spill with suspected source samples, it is possible to determine the responsible party.[26] High performance liquid chromatography (HPLC) has become the most widely used of all liquid chromatographic procedures. As in GLC, the stationary phase is a liquid immobilized on a solid support. The mobile phase is also a liquid, usually of considerably different polarity. The difference in polarity determines the partitioning between the mobile phase and the stationary phase. It would be prohibitively expensive to stock all the solvents that would be required to produce the desired difference in distribution ratios to effect a complete separation in all the possible combinations where it might be needed. It would be far more economical to stock only a few solvents which could be combined in various combinations to achieve favorable differences in distribution.

Because partitioning is important in a multitude of environmental, biological, ecological, and analytical events, and since partition coefficients can be closely approximated by the solubility of the solute in each phase, it is important to know the solubility of many different compounds. For this dissertation, the solubility of anthracene in the forty-five combinations of three alkanes, three ethers, and five different alcohols were studied. For each system, nineteen solutions were made and allowed to equilibrate for a minimum of three days. For each solution, four to eight measurements were taken,

sometimes days apart, to ensure the accuracy of the measurements. Because only a limited amount of space is available in the water baths to equilibrate the solutions, this significantly extends the time necessary to gather all the necessary data on any one given ternary system. In multicomponent systems, each additional component significantly increases the number of measurements that must be made. Even with modern instrumentation, the experimental measurements characterizing multicomponent systems become progressively more difficult, more expensive, and more time consuming to gather. It quickly becomes essential to develop good predictive models of solubility.

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CHAPTER II

REVIEW OF THE LITERATURE

Ideal and Nonideal Mixtures

There are two principal reasons for studying the properties of liquid mixtures. Liquid mixtures can be used to study the physical forces acting between two molecules of different species. Because it is difficult to interpret the properties of liquids in terms of intermolecular forces, the equilibrium and the transport properties of dilute gases are the principal sources of that kind of information. The second reason for studying liquid mixtures is that new properties appear which are not present in the pure substances.[1,2]

The ideal mixture does not exist in reality. The ideal mixture is a concept we fabricated in order to have a norm against which to compare the thermodynamic properties of real mixtures. Because mixtures of non-electrolytes, that is, mixtures that do not significantly conduct electricity, adhere rather closely to certain ideal laws of mixing, it often is possible to predict accurately their thermodynamic properties.

The composition of a mixture can be expressed in many ways. One common way to express the concentration of a solution is moles per unit volume, M. Another is to express the ratio of the number of moles of one component in a binary solution to the number of moles of a second component, n_1/n_2. Often, when there are more than two

components in the mixture, mole fraction is the means of expressing concentration. The mole fraction, χ, of component A is given by

$$\chi_A = n_A/(n_A + n_B + \ldots) \qquad \text{Equation 2.1}$$

where n_i is the number of moles of constituent *i* present in the solution. It follows from Equation 2.1 that the sum of the mole fractions for all the components in a mixture must equal one. Often the volume fraction, ϕ, given by

$$\phi_A = n_A V_A/(n_A V_A + n_B V_B + \ldots) \qquad \text{Equation 2.2}$$

is defined in terms of the molar volumes of the pure liquid components, V_i, and is calculated by dividing the molecular weight by the density.[3] Volume fraction compositions are temperature dependent, however, in most solution models the temperature dependence is ignored in order to simplify the computations. Similarly, most solution models assume that the excess volume change upon mixing is negligible, as does eq 2.2. Both approximations are generally very good, except in extreme cases of solution nonideality.

One of the early and simplest attempts to describe ideal mixtures is that of Raoult's law.

$$P_A/P_A^\circ = \chi_A \qquad \text{Equation 2.3}$$

where P_A = partial pressure of species A in the vapor

P_A° = pressure of the vapor above the pure component

χ_A = the mole fraction of A in the mixture

This law suggests that the chance of finding a molecule of A in the vapor, compared to the chance for the pure liquid, is equal to the fraction of molecules of A in the mixture.[4] Expressed another way,

$$P_A = \chi_A P_A^\circ \qquad \text{Equation 2.4}$$

the partial pressure of component, P_A, over an ideal solution, is equal to the vapor pressure of the pure component, P_A°, at the temperature of the solution times the mole fraction, χ_A, of component A in the liquid phase. Dalton's law of partial pressures, which states that the total pressure exerted by a mixture of gases is equal to the sum of the pressure that each gas exerts by itself, is expressed as[5]

$$P_{total} = P_A + P_B + P_C + \ldots \qquad \text{Equation 2.5}$$

Substituting Equation 2.4 into Equation 2.5 gives us the total vapor pressure for an ideal binary gas mixture above a liquid

$$P_{total} = \chi_A P_A^\circ + \chi_B P_B^\circ = \chi_A P_A^\circ + (1 - \chi_A) P_B^\circ = \chi_A (P_A^\circ - P_B^\circ) + P_B^\circ$$

Equation 2.6

Because P_A° and P_B° are constant for any system at a specified temperature, if the mixture is nearly ideal, then the total pressure dependence on the liquid phase composition is linear.[3] In mixtures of liquids, where the molecules of different species are significantly different in size, or where hydrogen bonding occurs between the species, there are negative deviations from Raoult's law. However, mixtures of water with a less polar solvent show positive deviations from Raoult's law. This is because water is a strongly self-associated liquid, and a second component tends to interfere with self-association. This is accompanied by a corresponding unfavorable change in enthalpy.

Thus, the interactions between molecules in the pure liquids and in mixtures often explain quantitatively the deviations from the ideal mixing laws.

For non-ideal mixtures, an activity coefficient, γ, is introduced into Raoult's law such that

$$P_A = \gamma_A \chi_A P_A^\circ \qquad \text{Equation 2.7}$$

The activity coefficient equals one in an ideal mixture. In non-ideal mixtures, the activity coefficient is a function of pressure, temperature, and composition. Using classical and statistical thermodynamics, the activity coefficient can be calculated theoretically only for simple systems. Usually, the activity coefficient must be determined experimentally. For nonelectrolyte solutions, data from the equilibrium of vapor-liquid systems often is used to determine activity coefficients and the testing of empirical or semi-empirical predictive methods.

The differences between the thermodynamic mixing parameters and the corresponding values for the ideal mixture provide convenient measures of the nonideality of liquid mixtures. The most important parameters are

$$G^E = \Delta G_{mix} - RT \Sigma \chi_i \ln \chi_i \qquad \text{Equation 2.8}$$

$$S^E = \Delta S_{mix} - R \Sigma \chi_i \ln \chi_i \qquad \text{Equation 2.9}$$

$$H^E = \Delta H_{mix} \qquad \text{Equation 2.10}$$

Excess functions are related by equations of the usual type

$$G^E = H^E - TS^E \qquad \text{Equation 2.11}$$

Each of these parameters will be nearly zero for mixtures of liquids that are very similar in their chemical composition. Rowlinson[1,2] cites numerous examples, showing that the

deviations from ideality of mixtures of simple liquids depends primarily on the differences in nonspecific interactions. These solutions have positive (endothermic) enthalpies of mixing. Mixtures of molecules that differ just slightly in dispersion forces, but greatly in size, exhibit negative deviations from Raoult's law by having positive entropies of mixing. Thus, it is possible to distinguish between two types of simple mixtures, with the transition between the two types being continuous. For mixtures of similar size molecules, the dominant factor is the enthalpy of mixing which increases as the relative size of the molecule increases. At the same time, the enthalpic effect is compensated for by a gradual increase in the value of ΔS^E.

Interactions between molecules also can cause deviations from ideality. When two polar liquids are mixed, various effects can occur. If the interactions between unlike molecules are stronger than those between like molecules, the enthalpy of mixing will be negative. However, the enthalpy of mixing will be positive if the interactions between unlike molecules are weaker. In fact, in the case of weaker interactions between unlike molecules, nonspecific interactions may be the dominating force. In mixtures of homologs, such as 1-butanol and 1-pentanol, the interactions between the two different kinds of molecules are comparable to the interactions between the same kinds of molecules. On the other hand, if we look at a mixture of acetone and chloroform,[6] the hydrogen bonding between the molecules of the two compounds probably accounts for the negative value of H^E. Since mixing is a randomizing process, ΔS_{mix} will be positive. Once again, hydrogen bonding plays a significant role in causing more order in the mixture than in an ideal system. This gives a negative S^E.

Flory[7,8] and Huggins[9,10] independently derived an expression for the entropy of mixing of polymer solutions, such that $\Delta S^E \neq 0$ in an athermal solution. An athermal solution is one whose components mix with no absorption or liberation of heat. The authors used the concept of a quasi-solid lattice for the liquid state. They assumed that all polymer molecules are of the same size and behave like a chain possessing a large number of equal-sized segments. In addition, each segment is identical in size to the solvent molecule. It occupies a single site. Adjacent segments occupy adjacent sites in the crystalline lattice.

The expression developed by Flory and Huggins for the change in Gibbs energy and entropy when an amorphous polymer mixes without synergistic effects is

$$\Delta G_{AB}^{mix} = -T\Delta S_{AB}^{mix} = RT[\chi_A \ln \phi_A + \chi_B \ln \phi_B] \qquad \text{Equation 2.12}$$

The symbols, ϕ_A and ϕ_B, represent the volume fractions for the solvent and the polymer, respectively. As a consequence, the Flory–Huggins solution model predicts negative deviations from Raoult's law for an athermal solution in which the molecules differ in size.

Since the Flory–Huggins model overestimates the number of possible configurations of the polymer, it is necessary to add a semi-empirical term for the enthalpy of mixing to eq 2.12. The excess enthalpy was assumed to be proportional to the volume of the solution and the product of the volume fractions. With this addition, the Flory–Huggins expression for real polymer solutions becomes

$$\Delta G_{AB}^{mix} = RT[\chi_A \ln \phi_A + \chi_B \ln \phi_B + \phi_A\phi_B(\chi_A + \chi_B m)]X$$

Equation 2.13

where the Flory interaction parameter, X, is determined by intermolecular forces between the molecules in solution. This includes interactions between pairs of solvent molecules and interactions between one polymer segment and one solvent molecule. The term, *m*, is set equal to the ratio of the molar volumes. The Flory interaction parameter is zero for athermal solutions and small for mixtures of chemically similar components.

Solid-Liquid Equilibria

The solubility of a solid in a liquid is strongly dependent upon the relative strengths of the intermolecular forces between the dissolved solute and the surrounding solvent molecules. A common saying among chemists comes from the Latin phrase *similis similibus solvuntur*[11-13] (like dissolves like). This is nothing more than an empirical statement of fact. In the absence of specific interactions, intermolecular forces between chemically similar species lead to a smaller endothermic enthalpy of solution than those between dissimilar species. Dissolution must be accompanied by a decrease in the Gibbs energy. For this reason, a low endothermic enthalpy is preferable to a large one. In addition to the intermolecular forces between solute and solvent, several other factors play a role in determining the solubility of a solid in a liquid.

Three, and sometimes, four other factors[14] contribute to determining whether or not a solid will dissolve:

(a) breaking of the solute-solute interactions in the crystalline lattice;

(b) the breaking of solvent-solvent interactions, often referred to as cavity formation;

(c) the formation of solute-solvent interactions, and

(d) the perturbation of solvent-solvent interactions in the immediate vicinity of the solute, as in solvent structuring.

Each of these four contributions may be divided further into specific chemical (complexation) and nonspecific (simple dispersion) interactions. Specific interactions result from a specific geometric orientation of one molecule with respect to adjacent molecules. They arise from charge transfer species, hydrogen bond formation, and strong dipole-dipole interactions. A random distribution of molecules throughout the entire solution best characterizes nonspecific interactions. Specific interactions occur only in complexing systems, whereas nonspecific interactions occur in both complexing and noncomplexing systems. Systems containing specific interactions and/or nonspecific interactions deviate from ideality. The activity coefficient, γ, reflects the intermolecular forces between the solute and the solvent. Large negative ($\gamma < 1$) or large positive ($\gamma > 1$) deviations usually accompany specific interactions. However, systems containing only nonspecific interactions usually are characterized by small to moderate positive deviations from ideality. For this reason, solubility tends to be enhanced for negative deviations and decreased for positive deviations.

Experimental evidence has shown us that isomers do not have the same solubility in a given solvent all the time. For example, phenanthrene is approximately 25 times more soluble in benzene than is anthracene, even though both solids are chemically similar. The reason for this large solubility difference is the often overlooked, but the governing, thermodynamic criterion

$$a_A = a_A^* \qquad \text{Equation 2.14}$$

that the activity of any solute, A, must be the same in both phases, or

$$a_A^* = \gamma_A \chi_A a_A^\circ \qquad \text{Equation 2.15}$$

where * represents the pure solid; χ_A is the mole fraction solubility of the solute in the solvent, γ_A is the liquid phase activity coefficient, and a_A° = the standard state activity to which γ_A refers. The selection of the standard state, a_A°, is arbitrary. The only thermodynamic requirement is that it must be at the same temperature as the saturated solution. For convenience, it is advantageous to define the standard state activity of the pure supercooled liquid, $a_A^*(l)$, at the temperature of the solution and at some specified pressure. This hypothetical standard state is one whose properties can be calculated with reasonable accuracy, provided the temperature of the solution is close to the triple point (melting point) temperature of the solute, T_{MP}. This explains why phenanthrene and anthracene have different solubilities in simple hydrocarbon solvents, such as hexane or benzene.[3] The triple point temperatures of these two solids are different because of structural differences.

It may be appropriate to note, at this point, that the standard state for the solute differs from the normal thermodynamic convention used for electrolyte salts. In the case of electrolyte salts, the activity of the solid generally is taken as unity. For nonelectrolyte solutes, the subnormal liquid is taken as the standard state. Since most thermodynamic models originally were developed for the mixing of two or more liquids, the selection of the subcooled liquid as the solute standard state facilitates thermodynamic modeling. This allows the change in entropy to be discussed conveniently in terms of the number of

possible ways of arranging the various molecules on a fixed lattice cell. Molecules on the lattice cell would have approximately the same degree of mobility as the molecules in pure liquids. This is different from a solid where the molecules are more rigidly fixed in space.

A system at equilibrium, under a given set of conditions, is said to be in a definite state. In this definite state, each of its properties has a definite value. Thermodynamic properties are state functions. They are chosen so they depend only on the initial and final states of the solution. Thermodynamic properties are independent of the pathway by which a solution gets from one state to another.[15] Using the following three-step Hess' Law thermodynamic cycle, the standard state activitiy of a solid solute can be computed:

Step I: Solute A (solid, T) $\rightarrow$ Solute A (solid, T_{MP})

Step II: Solute A (solid, T_{MP}) $\rightarrow$ Solute A (liquid, T_{MP})

Step III: Solute A (liquid, T_{MP}) $\rightarrow$ Solute A (supercooled liquid, T)

with the overall process being

Solute A (solid, T) $\rightarrow$ Solute A (supercooled liquid, T)

and for the overall process

$$\Delta G = RT \ln a_A^{solid} = \Delta G_I + \Delta G_{II} + \Delta G_{III} \qquad \text{Equation 2.16}$$

If we assume the difference in the heat capacities between the solid and the supercooled liquid remains constant over the temperature range from T to T_{MP}, we obtain the following expression

$$\ln a_A^{solid} = \ln(\gamma_A \chi_A) =$$

$$- \Delta H^{fus}(T_{MP} - T)/(RTT_{MP}) + \Delta C_P(T_{MP} - T)/RT - (\Delta C_P/R) \ln(T_{MP}/T)$$

Equation 2.17

for the solubility of a crystalline solute in a liquid solvent. If the solid undergoes a phase transition, the expression for a_A^{solid} must include additional term(s).

Two conclusions can be made from Equation 2.17. As these conclusions rigorously apply to ideal solutions ($\gamma_i = 1$), they only can be applied to real solutions that do not deviate excessively from ideal behavior. However, they do serve as useful guides regarding the solubility of solids in liquids.

(a) For a given solid-solvent system, the solubility increases with increasing temperature. The rate of increase is approximately proportional to the enthalpy of fusion and, to a first approximation, does not depend on the melting point (triple point) temperature, i. e., $\partial \ln(\gamma_A \chi_A)/\partial T \approx \Delta H^{fus}/RT^2$.

(b) For a given solvent at a fixed temperature, if two solids have a similar entropy of fusion, then the solid with the lower melting point temperature has the higher solubility. Similarly, if two solids have about the same melting point temperature, then the one with the lower enthalpy of fusion has the higher solubility.[3] Let us return to our example of the huge difference in the solubility of phenanthrene and anthracene[13] (χ^{sat} = 0.2068 and 0.0081, respectively, in benzene). In addition to the significant structural differences that cause differences in the triple point temperatures of the two solids (101°C and 216.4°C, respectively)[16], the ratios of the fugacities (to which the activity coefficients refer) at the same temperature T also differ for the two solutes. Similarly, benz[a]anthracene and naphthacene have an approximate 25-fold difference in aqueous mole fraction solubility (9.40

x 10^{-10} versus 3.70 x 10^{-11}, respectively), along with vastly different melting points (182.0°C versus 357.0°C, respectively). On the other hand, the two benzofluoranthene isomers, benzo[b]fluoranthene and benzo[j]fluoranthene[13] have roughly the same aqueous solubility (1.07 x 10^{-10} and 1.78 x 10^{-10}, respectively) and melting temperatures (168.0°C and 166.0°C, respectively).

The Scatchard–Hildebrand Model

Because nonelectrolyte solutions rarely are ideal, activity coefficients must be introduced to describe thermodynamically observed solution behavior. Several equations have been proposed to predict activity coefficients. There are far more published equations describing noncomplexing and complexing solutions, as well as equations describing group contributions based on functional groups present, than can be presented in this dissertation. Therefore, only those solution models that will be used later in interpreting the measured anthracene solubility in the ternary mixtures we investigated will be discussed.

The Scatchard–Hildebrand model[17-21] defines a new parameter, c, according to

$$c_i = \Delta U_i^{vap}/V_i \qquad \text{Equation 2.18}$$

where the energy ΔU_i^{vap} is required for the isothermal vaporization of the saturated liquid to the ideal gas state. This parameter, c, is referred to as the cohesive energy density.

Hildebrand and Scatchard generalized eq 2.18 to one mole of a binary liquid mixture

$$-(U_{liq} - U_{id\,g})_{bm} = (c_A V_A^2 \chi_A^2 + 2c_{AB}\chi_A V_A \chi_B V_B + c_B V_B^2 \chi_B^2)/(\chi_A V_A + \chi_B V_B)$$

Equation 2.19

where bm denotes the binary mixture, and V_A is the molar volume of a pure liquid.

To simplify the notation, the symbols ϕ_A and ϕ_B, which designate the ideal volume fractions of components A and B, are introduced

$$\phi_A = \chi_A V_A/(\chi_A V_A + \chi_B V_B) \qquad \text{Equation 2.20}$$

$$\phi_B = \chi_B V_B/(\chi_A V_A + \chi_B V_B) \qquad \text{Equation 2.21}$$

Making these substitutions, eq 2.19 becomes

$$-(U_{liq} - U_{id\,g})_{bm} = (\chi_A V_A + \chi_B V_B)(c_A \phi_A^2 + 2c_{AB}\phi_A\phi_B + c_B\phi_B^2)$$

Equation 2.22

The molar energy change of mixing, which is also the excess energy of mixing, is defined by

$$\Delta U_{AB}^E = U_{bm} - \chi_A U_A^\circ - \chi_B U_B^\circ \qquad \text{Equation 2.23}$$

Utilizing the relationship for ideal gases

$$\Delta U_{id}^E = U_{id\,g} - \chi_A U_A^\circ - \chi_B U_B^\circ = 0 \qquad \text{Equation 2.24}$$

combine eq 2.18 for each component and eq 2.22 to give

$$\Delta U_{AB}^E = (U_{bm} - \chi_A U_A^\circ - \chi_B U_B^\circ) - (U_{id\,g} - \chi_A U_A^\circ - \chi_B U_B^\circ) =$$

$$(c_A + c_B - 2c_{AB})\phi_A\phi_B(\chi_A V_A + \chi_B V_B) \qquad \text{Equation 2.25}$$

Scatchard and Hildebrand made these assumptions:

(a) The energy of the binary liquid mixture (relative to the ideal gas at the same temperature and composition) can be expressed as a quadratic function of the volume fractions, which also implies that the volume of the

binary liquid mixture is given by the ideal molar volume approximations (i.e., $\chi_A V_A + \chi_B V_B$).

(b) For molecules whose forces of attraction result primarily from dispersion forces, there is a simple relationship between the cohesive density parameters, c_A, c_B, and c_{AB}:

$$c_{AB} = (c_A c_B)^{1/2} \qquad \text{Equation 2.26}$$

The constants, c_A and c_B, refer to binary interactions between like molecules, whereas the constant, c_{AB}, refers to interactions between unlike molecules.

(c) At constant temperature and pressure, the excess entropy of mixing vanishes, i.e., $\Delta S_{AB}^{E} = 0$.

(d) The enthalpy of mixing remains constant as the temperature is varied. This follows from assumption c, that, at constant composition, the logarithm of each activity coefficient must be inversely proportional to the absolute temperature.

Substituting eq 2.26 into eq 2.25 gives

$$\Delta U_{AB}^{E} = \phi_A \phi_B (\chi_A V_A + \chi_B V_B)(\delta_A - \delta_B)^2 \qquad \text{Equation 2.27}$$

where $\delta_A = c_A^{1/2} = (\Delta U_A^{vap}/V_A)^{1/2}$, and $\delta_B = c_B^{1/2} = (\Delta U_B^{vap}/V_B)^{1/2}$. The positive square of c is given the special symbol, δ, which is called the solubility parameter. Elimination of the excess entropy and volume gives

$$\Delta G_{AB}^{E} = \Delta H_{AB}^{E} = \Delta U_{AB}^{E} = \phi_A \phi_B (\chi_A V_A + \chi_B V_B)(\delta_A - \delta_B)^2$$

Equation 2.28

With these assumptions, the Scatchard–Hildebrand solubility parameter model provides reasonable estimates of solute solubility in systems containing only nonspecific interactions

$$RT \ln(a_A^{solid}/\chi_A) = V_A(1 - \phi_A)^2(\delta_A - \delta_{solvent})^2 \qquad \text{Equation 2.29}$$

where δ_A and $\delta_{solvent}$ refer to the solubility parameters of the supercooled liquid solute and solvent, respectively; V_A is the molar volume of the supercooled liquid solute, χ_A is the saturation mole fraction solubility, ϕ_A is the solute's volume fraction solubility calculated, using the ideal molar volume approximations. Because of the assumption that the cohesive energy corresponding to the interactions between dissimilar molecules is given by the geometric average of the cohesive energy densities corresponding to interactions between similar molecules (eq 2.26), the Hildebrand–Scatchard equations always predict positive deviations from Raoult's law.

Even though the solubility parameters, δ_A and δ_B, are functions of temperature, the difference between these parameters, $\delta_A - \delta_B$, is frequently nearly independent of temperature. This is a reasonable assumption to make for many solutions of nonpolar liquids, provided the temperature range is narrow, and the solution does not approach critical conditions.

For many pure solvents, the solubility parameters and liquid molar volumes are tabulated in the literature by Hoy[22] and Barton[23]. When these properties are not tabulated already for the desired solvent, they can be calculated from density and vapor pressure measurements on the pure liquid. On the other hand, the molar volumes of supercooled liquid solutes are estimated either by group contribution methods or by

experimentally determined apparent partial molar volumes in the desired solvent. Solubility parameters of the supercooled liquid of interest can be obtained indirectly from solubility measurements, or they can be estimated by group contribution methods.

Simplicity is one the main advantages of the Scatchard–Hildebrand model. Fortunately, this simplicity is retained when the model is extended to liquid solutions having more than two components. The derivation of the multi-component case is completely analogous to that for a binary system. To illustrate how this is done, the molar energy of a ternary mixture is written as

$$-(U_{liq} - U_{i\,g})_{tm} = (\chi_A{}^2 V_A{}^2 c_A + \chi_B{}^2 V_B{}^2 c_B + \chi_C{}^2 V_C{}^2 c_C + 2\chi_A\chi_B V_A V_B c_{AB} +$$

$$2\chi_A\chi_C V_A V_C c_{AC} + 2\chi_B\chi_C V_B V_C c_{BC})/(\chi_A V_A + \chi_B V_B + \chi_C V_C)$$

$$= (\chi_A V_A + \chi_B V_B + \chi_C V_C)(\phi_A{}^2 c_A + 2\phi_A\phi_B c_{AB} + \phi_B{}^2 c_B + \phi_C{}^2 c_C + 2\phi_A\phi_C c_{AC} + 2\phi_B\phi_C c_{BC})$$

Equation 2.30

where tm is the ternary mixture. The volume fraction of component A is defined by

$$\phi_A = \chi_A V_A/(\chi_A V_A + \chi_B V_B + \chi_C V_C) \qquad \text{Equation 2.31}$$

and the excess energy of mixing is defined by

$$\Delta U_{ABC}{}^E = U_{tm} - \chi_A U_A{}^\circ - \chi_B U_B{}^\circ - \chi_C U_C{}^\circ \qquad \text{Equation 2.32}$$

Combining eqs 2.30-2.32, the excess energy of mixing in terms of the cohexive energy densities is written as

$$\Delta U_{ABC}{}^E = (\chi_A V_A + \chi_B V_B + \chi_C V_C)x$$

$$[\phi_A\phi_B(c_A + c_B - 2c_{AB}) + \phi_A\phi_C(c_A + c_C - 2c_{AC}) + \phi_B\phi_C(c_B + c_C - 2c_{BC})]$$

Equation 2.33

Assuming the cohesive energy density, c_{ij}, is given by the geometric mean

$$c_{ij} = (c_i c_j)^{1/2}$$

and that

$$\Delta S_{ABC}^{E} = \Delta V_{ABC}^{E} = 0$$

the excess Gibbs energy (or the excess enthalpy) of a ternary liquid mixture can be expressed in terms of solubility parameters

$$\Delta U_{ABC}^{E} = \Delta G_{ABC}^{E} = \Delta H_{ABC}^{E} = (\chi_A V_A + \chi_B V_B + \chi_C V_C)x$$

$$[\phi_A\phi_B(\delta_A - \delta_B)^2 + \phi_A\phi_C(\delta_A - \delta_C)^2 + \phi_B\phi_C(\delta_B - \delta_C)^2] \qquad \text{Equation 2.34}$$

Inspection of eq 2.34 reveals that for regular ternary solutions obeying this model equation, the properties of the contributive binary systems would obey (per mole of solution)

$$\Delta G_{AB}^{E} = \Delta H_{AB}^{E} = \Delta U_{AB}^{E} = (\chi_A V_A + \chi_B V_B)\phi_A\phi_B(\delta_A - \delta_B)^2$$

Equation 2.35

where the mole fraction compositions (χ_A°, χ_B°) are calculated now as if the third component were not present

$$\chi_A^\circ = 1 - \chi_B^\circ = \chi_A^\circ/(\chi_A^\circ + \chi_B^\circ) \qquad \text{Equation 2.36}$$

Suitable manipulation of eqs 2.35 gives us the following expression for the excess Gibbs energy of a ternary mixture.

$$\Delta G_{ABC}^{E} = (\chi_A + \chi_B)(\phi_A + \phi_B)\Delta G_{AB}^{E} + (\chi_A + \chi_C)(\phi_A + \phi_C)\Delta G_{AC}^{E} +$$

$$(\chi_B + \chi_C)(\phi_B + \phi_C)\Delta G_{BC}^{E}$$

Equation 2.37

The Scatchard–Hildebrand solubility parameter approach is extended to binary solvent mixtures by defining the solubility parameter of a solvent, $\delta_{solvent}$,

$$\delta_{solvent} = (\phi_B\delta_B + \phi_C\delta_C)/(\phi_B + \phi_C) = \phi_B^{\circ}\delta_B + \phi_C^{\circ}\delta_C \quad \text{Equation 2.38}$$

as a volume fraction average of the solubility parameters of the two pure solvents, δ_B and δ_C. The superscript ° indicates that the solvent composition is calculated as if the solute were not present. This approach relates the solubility of a solute in a given solvent, either pure or mixed, to the bulk properties of the pure components. Even though this application of the solubility parameter theory requires only a minimal number of experimental observations, a more flexible expression for binary solvent systems can be derived by replacing the individual δ_i values with the measured solubilities in the pure solvents and the measured thermodynamic excess properties of the solvent mixture.

To incorporate direct experimental observations into the basic solubility parameter model, first substitute eq 2.38 into eq 2.29

$$(1 - \phi_A)^{-2}RT \ln(a_A^{solid}/\chi_A) = V_A(\phi_B^{\circ}\delta_B + \phi_C^{\circ}\delta_C - \delta_A)^2 \quad \text{Equation 2.39}$$

and multiplying out the squared term

$$(1 - \phi_A)^{-2}RT \ln(a_A^{solid}/\chi_A) = V_A[\phi_B^{\circ}(\delta_B - \delta_A)^2 + \phi_C^{\circ}(\delta_C - \delta_A)^2 - \phi_B^{\circ}\phi_C^{\circ}(\delta_B - \delta_C)^2] \quad \text{Equation 2.40}$$

allows the incorporation of direct experimental observations into the basic solubility parameter model. For model systems obeying this expression, inspection of eq 2.39 shows us that the saturation solubility of the solute in a pure solvent (components B and C) is described by

$$(G_A^E)_i^{\infty} = (1 - \phi_A)^{-2}RT \ln(a_A^{solid}/\chi_A) = V_A(\delta_i - \delta_A)^2 \quad \text{Equation 2.41}$$

where the small subscripts, i = B and i = C, are used to distinguish the properties of the solute in a pure solvent from those in the binary solvent system. In the same manner, the

excess Gibbs energy of the binary solvent mixture can be written as eq 2.35 in terms of solubility parameters. If we treat the quantity $(\delta_B - \delta_C)^2$ as an empirically determined interaction parameter instead of as the evaluation of solubility parameters from energies of vaporization, then eq 2.28 is remarkably successful for excess enthalpies and free energies. Since there are no restrictions placed on the value of $(\delta_B - \delta_C)^2$, positive and negative deviations from Raoult's law are found.

By combining eqs 2.39 - 2.41, we find that the solubility of a solute in binary solvent mixtures containing only nonspecific interactions is

$$RT \ln(a_A^{solid}/\chi_A) = (1 - \phi_A)^{-2}[\phi_B^\circ (G_A^E)_B^\infty + \phi_C^\circ (G_A^E)_C^\infty - V_A(\chi_B^\circ V_B + \chi_C^\circ V_C)^{-1} G_{BC}^E]$$

Equation 2.42

a volume fraction average of the solute's properties in the two pure solvents, $(G_A^E)_B^\infty$ and $(G_A^E)_C^\infty$, and a contribution due to the nonmixing of the solvent pair by the presence of the solute.

Nearly Ideal Binary Solvent (NIBS) Model

The NIBS model was developed by Bertrand and co-workers[24-28] to describe the thermodynamic properties of a solute in binary solvent mixtures. It has been successful in predicting enthalpies of solution and solubilities in mixed solvents in which only nonspecific interactions occur. The basic principles of this model, pertaining to chemical potential or the partial molar Gibbs free energy of a solute, will be reviewed to identify the assumptions made in the derivation of the predictive equations.

In the NIBS approach, it is assumed that only two-body interactions are important. Three-body, four-body, etc. interactions are ignored. Within this framework, the excess Gibbs energy of mixing, ΔG_{ABC}^{E}, is given by

$$\Delta G_{ABC}^{E} = (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)^{-1}(n_A\Gamma_A n_B\Gamma_B A_{AB} + n_A\Gamma_A n_C\Gamma_C A_{AC} + n_B\Gamma_B n_C\Gamma_C A_{BC})$$

Equation 2.43

in which Γ_i is a weighting factor describing the likelihood of molecular interactions involving component *i*, and A_{ij} is a binary interaction parameter that is independent of composition. Through differentiation of eq 2.43, the corresponding partial molar excess Gibbs energy of the solute (component A) can be expressed as a weighted mole fraction average of the properties in the pure solvents, $(G_A^{E})_B^{\infty}$ and $(G_A^{E})_C^{\infty}$, and a contribution due to the unmixing of the binary solvent pair because of the presence of the solute

$$(G_A^{E})^{\infty} = f_B^{\circ}(G_A^{E})_B^{\infty} + f_C^{\circ}(G_A^{E})_C^{\infty} - \Gamma_A(\chi_B^{\circ}\Gamma_B + \chi_C^{\circ}\Gamma_C)^{-1}\Delta G_{BC}^{E}$$

Equation 2.44

where

$$f_B^{\circ} = 1 - f_C^{\circ} = n_B\Gamma_B/(n_B\Gamma_B + n_C\Gamma_C)$$

and

$$\chi_B^{\circ} = 1 - \chi_C^{\circ} = n_B/(n_B + n_C)$$

In eq 2.44 and subsequent equations, the superscript, $^{\infty}$, indicates an extrapolated value for the infinitely dilute solution ($f_A = 0$). Most of the specific elements of the model eq. 2.43 were removed. Only the weighting factors remain. Reasonable estimates have been developed for the weighting factors, and previous researchers in the Acree

group have compared the predicted thermodynamic excess properties of the solute in binary solvent mixtures to experimental data.

Weighting factors represent a measure of the skew of the binary thermodynamic excess property from mole fraction symmetry. They only can be evaluated relative to one another as the ratio of two weighting factors (Γ_i/Γ_j). Other researchers previously have proposed several methods for the evaluation of these weighting factors from the thermodynamic properties of binary mixtures.[27-30] In the case of solute solubility where only a single data point is associated with each solute-solvent pair, many of these methods are not applicable. To avoid calculating these weighting factors, simple approximations can be made by:

a) substituting the molar volume for the weighting factor for each component
b) setting the weighting factors for each component equal to each other, and
c) substituting the surface area for the weighting factor for each component.

For directly observed excess properties such as volume and enthalpy, the equations for thermodynamic excess properties are relatively straight-forward to develop. However, in the case of the Gibbs energy, it is the total free energy of mixing that is determined experimentally. The excess value must be calculated as the difference between the observed value and the value of an ideal solution:

$$\Delta G^{mix} = RT \Sigma n_i \ln \chi_i + \Delta G^E \qquad \text{Equation 2.45}$$

For mixtures containing molecules with considerable differences in molar volumes, general mixing equations which possess the mathematical form of eq 2.43 more

accurately describe differences between the total free energy of mixing and that predicted from the Flory–Huggins expression:

$$\Delta G^{mix} = RT \Sigma n_i \ln \phi_i + \Delta G^{FH} \qquad \text{Equation 2.46}$$

For a binary mixture, the difference between the excess Gibbs energy and the Flory–Huggins excess Gibbs energy is given by

$$\Delta G_{AB}{}^{FH} = \Delta G_{AB}{}^{E} + RT[\ln(\chi_A V_A + \chi_B V_B) - \chi_A \ln V_A - \chi_B \ln V_B]$$

Equation 2.47

The mathematical treatment of these general mixing equations leads to two general expressions for estimating the partial molar excess Gibbs energy of a solute at mole fractions low enough to be near infinite dilution in a binary solvent

$$\Delta G_A{}^{E} = (1 - f_A)^2[f_B{}^{\circ}(\Delta G^{E}{}_A)_B{}^{\infty} + f_C{}^{\circ}(\Delta G^{E}{}_A)_C{}^{\infty} - \Gamma_A(\chi_B{}^{\circ}\Gamma_B + \chi_C{}^{\circ}\Gamma_C)^{-1}(\Delta G^{E}{}_{BC})]$$

Equation 2.48

and

$$\Delta G_A{}^{FH} = (1 - f_A)^2[f_B{}^{\circ}(\Delta G_A{}^{FH})_B{}^{\infty} + f_C{}^{\circ}(\Delta G_A{}^{FH})_C{}^{\infty} - \Gamma_A(\chi_B{}^{\circ}\Gamma_B + \chi_C{}^{\circ}\Gamma_C)^{-1}(\Delta G_{BC}{}^{FH})]$$

Equation 2.49

The term $\Delta G_A{}^{FH}$ represents an excess partial molar free energy of the solute as it relates to an ideal mixing equation based on volume fractions (eq 2.12) rather than mole fractions (eq 2.8).

The chemical potential of the solute in binary solvent mixtures can be related to the solubility through basic thermodynamic relationships

$$\Delta G_A{}^{E} = RT \ln(a_A{}^{solid}/\chi_A{}^{sat}) \qquad \text{Equation 2.50}$$

$$\Delta G_A{}^{FH} = RT\{\ln(a_A{}^{solid}/\phi_A{}^{sat}) - [1 - (V_A{}^{\circ}/V_{sol})]\} \qquad \text{Equation 2.51}$$

where $V_A°$ is the molar volume of the solute in the liquid state at the desired temperature, and a_A^{solid} is the activity of the solute with reference to the hypothetical liquid supercooled below the normal melting point.

Based upon the definitions of mixture ideality and weighting factor approximations, Acree and Bertrand[27-29] derived the following three NIBS expressions:

$$RT \ln(a_A^{solid}/\chi_A^{sat}) = (1 - \chi_A)^2[\chi_B°(\Delta G_A^E)_B^\infty + \chi_C°(\Delta G_A^E)_C^\infty - \Delta G_{BC}^E]$$

Equation 2.52

$$RT \ln(a_A^{solid}/\chi_A^{sat}) =$$

$$(1 - \phi_A^{sat})^2[\phi_B°(\Delta G_A^E)_B^\infty + \phi_C°(\Delta G_A^E)_C^\infty - V_A°(\chi_B°V_B + \chi_C°V_C)^{-1}\Delta G_{BC}^E]$$

Equation 2.53

and

$$RT\{ \ln(a_A^{solid}/\phi_A^{sat}) - (1 - \phi_A^{sat})[1 - V_A°/(\chi_B°V_B + \chi_C°V_C)]\} =$$

$$(1 - \phi_C^{sat})^2[\phi_A°(\Delta G_C^{FH})_A^\infty + \phi_B°(\Delta G_C^{FH})_B^\infty - V_A(\chi_B°V_B + \chi_C°V_C)^{-1}\Delta G_{BC}^{FH}]$$

Equation 2.54

for predicting solubilities in binary solvent mixtures. In these three equations, the solute is component A, ϕ_i is the volume fraction of component *i*, and V_i is the molar volume of component *i*.

The Scatchard–Hildebrand solubility parameter theory can be used to derive Eq 2.53 by eliminating the three δs with the measured experimental solubilities in the pure solvents and the thermodynamic excess properties of the binary solvent. The NIBS treatment is more general, and no restrictions are placed on the numerical values of the

binary interaction parameters. Acree and coworkers[25,27,28,31] have shown that eqs 2.53 and 2.54 generate reasonable estimates (±5%) for experimental solubilities of benzil, naphthalene, iodine, carbazole, anthracene, pyrene, and thianthrene in noncomplexing solvent systems. The superiority of expressions based on molar volumes suggests that the relative sizes of the molecules are an important consideration. Because surface areas are a different measure of molecular size, it may be valuable to use surface areas as weighting factors. The introduction of molecular surface areas (A_i) into the basic NIBS model (eq 2.43) leads to the development of two more predictive expressions

$$RT \ln(a_A^{solid}) = (1 - \theta_A^{sat})^2[\theta_B^{\circ}(\Delta G_A^{E})_B^{\infty} + \theta_C^{\circ}(\Delta G_A^{E})_C^{\infty} - A_A(\chi_B^{\circ}A_B + \chi_C^{\circ}A_C)^{-1}\Delta G_{BC}^{E}]$$

Equation 2.55

and

$$RT\{ \ln(a_A^{solid}/\phi_A^{sat}) - (1 - \phi_A^{sat})[1 - V_A^{\circ}/(\chi_B^{\circ}V_B + \chi_C^{\circ}V_C)]\} =$$

$$(1 - \theta_A^{sat})^2[\theta_B^{\circ}(\Delta G_A^{FH})_B^{\infty} + \theta_C^{\circ}(\Delta G_A^{FH})_C^{\infty} - A_A(\chi_B^{\circ}A_B + \chi_C^{\circ}A_C)^{-1}\Delta G_{BC}^{FH}]$$

Equation 2.56

depending on whether Raoult's law (eq 2.55) or the Flory–Huggins model (eq 2.56) is used to define solution ideality.

Acree and Rytting[32] noted that eq 2.55, based on surface areas as weighting factors for the excess free energies relative to Raoult's law, seems to be the most applicable predictive expression with an overall average root-mean-square (rms) deviation of about 1.7%. Conflicting values of ΔG_{BC}^{E} were reported for the benzene + n-heptane system, resulting in the maximum error of 7.5% for a single data point. The primary advantage of eq 2.55 over expressions based on molar volumes (eqs 2.53 and

2.54) is its applicability to anthracene and pyrene solubilities in solvent mixtures containing either benzene, methylbenzene, or 1,4-dimethylbenzene. Excluding these systems, eqs 2.53 and 2.54 are slightly better than equations based on surface areas.

It is difficult to gauge whether weighting factors are better approximated with molar volumes or surface areas. Because of the simplicity of the calculations and the readily available molar volumes, eq 2.53 is preferred. Some support for this form can be found in its adaptability to the Scatchard–Hildebrand solubility parameter theory. Similar support for eqs 2.55 and 2.56 is found in correlations of partition coefficients with surface areas and in several semi empirical expressions developed for predicting liquid-vapor equilibrium. Equation 2.55 also is applicable to polymer solutions. It is ideally suited to both molarity-based equilibrium constants and gas-liquid partition coefficients. Chiou and Manes[29,33] have shown that eq 2.55, based upon the Flory–Huggins model, is a more realistic description of ideality in systems having molecules of moderate size disparity.

The Combined NIBS/Redlich Kister

Mathemetical Representation

An early proposed expression for the excess energy of a ternary mixture, consisting of components A, B, and C, was developed by Redlich and Kister[34] in 1948.

$$\Delta G_{ABC}^{E} = \chi_A\chi_B\,\Sigma(G_v)_{AB}(\chi_A - \chi_B)^v + \chi_A\chi_C\,\Sigma(G_v)_{AC}(\chi_A - \chi_C)^v + \chi_B\chi_C\,\Sigma(G_v)_{BC}(\chi_B - \chi_C)^v$$

Equation 2.57

This expression has provisions for additional ternary parameters. The binary reduction of this expression

$$\Delta Z_{AB}^{E} = \chi_A \chi_B \Sigma (Z_v)_{AB} (\chi_A - \chi_B)^v \qquad \text{Equation 2.58}$$

is used mathematically to represent excess properties and physical properties of binary mixtures. Initially, this expression was popular because the first parameter could be determined conveniently by multiplying the experimental value χ_A by four. Since computers were not available in the 1940s, most experimental data was presented graphically in the literature. Equation 2.57 was a means to transmit data from the experimentalist to the chemical engineer. Many of the ΔG^E values used by Acree and coworkers for NIBS solubility predictions was reported in the chemical literature in the form of the Redlich–Kister equation[35,36].

The expressions for predicting the thermodynamic properties of ternary solvent systems have served as the point of departure for mathematical representation of experimental excess enthalpy and excess volume data. Differences between predicted and observed values are expressed as

$$(\Delta Z_{ABC}^{E})^{exp} - (\Delta Z_{ABC}^{E})^{calc} = \chi_A \chi_B \chi_C Q_{ABC} \qquad \text{Equation 2.59}$$

with Q-functions of varying complexity. The experimental data can be represented adequately by a power series expansion for most systems:

$$Q_{ABC} = A_{ABC} + \Sigma B_{AB}^{i} (\chi_A - \chi_B)^i + \Sigma B_{AC}^{j} (\chi_A - \chi_C)^j + \Sigma B_{BC}^{k} (\chi_B - \chi_C)^k$$

Equation 2.60

The summations in eq 2.60 extend over the number of curve-fit parameters that is needed to describe satisfactorily the experimental data. Experimental data rarely is determined

with sufficient precision to justify more than a few parameters. As part of a study of solute solubilities in binary solvent mixtures, Acree and Zvaigzne[36] examined possible mathematical representations based on the Combined NIBS/Redlich–Kister Equation

$$\ln \chi_A^{sat} = \chi_B^\circ \ln (\chi_A^{sat})_B + \chi_C^\circ \ln (\chi_A^{sat})_C + \chi_B^\circ \chi_C^\circ \Sigma S_i (\chi_B^\circ - \chi_C^\circ)^i$$

Equation 2.61

with the S_i parameter being determined from analyzing measured solubility data by using a method of least squares. Equation 2.61 is rearranged to the following mathematical form

$$[\ln \chi_A^{sat} - \chi_B^\circ \ln(\chi_A^{sat})_B - \chi_C^\circ \ln(\chi_A^{sat})_C] / (\chi_B^\circ \chi_C^\circ) = \Sigma S_i (\chi_B^\circ - \chi_C^\circ)^i$$

Equation 2.62

The right-hand side is a simple polynomial in ($\chi_B^\circ - \chi_C^\circ$). The Redlich–Kister summation term starts at $i = 0$, containing as many "curve-fit" S_i parameters as needed to describe the experimental data. It should allow this model to describe adequately the larger solubility ranges encountered in systems containing strong solute-solvent complexation.

The Combined NIBS/Redlich–Kister equation originally was presented in the literature as an empirical expression for the mathematical representation of isothermal solubility data for solutes dissolved in binary solvent mixtures. Subsequently, Acree[37] derived the expression from the two- and three-body interactional solution model developed by Hwang et al.[38] Hwang et al. expressed the excess molar Gibbs energy of a ternary mixture in terms of

$$\Delta G^E = \chi_A\chi_B(a_0^{AB} + a_1^{AB}\chi_A^3 + a_2^{AB}\chi_B^3) +$$

$$\chi_A\chi_C(a_0^{AC} + a_1^{AC}\chi_A^3 + a_2^{AC}\chi_C^3) + \chi_B\chi_C(a_0^{BC} + a_1^{BC}\chi_B^3 + a_2^{BC}\chi^3_C)$$

Equation 2.63

the six possible binary interactions and the ten possible ternary interactions. The parameters a_i^{AB}, a_i^{AC}, and a_i^{BC} represent the interactions. Through differentiation with respect to the number of moles of solute and series of algebraic manipulations, Acree was able to express the solubility of a crystalline nonelectrolyte solute in a binary solvent mixture as

$$\mu_A - \mu_A^\circ = RT \ln a_A^{solid} = RT \ln \chi_A^{sat} + \chi_B^0[a_0^{(AB)} + a_2^{(AB)}\chi_B^{03}]$$

$$+ \chi_C^0[a_0^{(AC)} + a_2^{(AC)}\chi_C^{03}] - \chi_B^0\chi_C^0[a_0^{(BC)} + 4a_0^{(BC)}\chi_B^{03} + 4a_2^{(BC)}\chi_C^{03}]$$

Equation 2.64

Mole fractions, χ_i^o, refer to the initial composition of the binary solvent mixture calculated as if the solute was not present, and a_A^{solid} denotes the activity of the solid solute, as defined by eq 2.17.

For model systems obeying eq 2.60, the $a_0^{(AB)}$ and $a_2^{(AC)}$, interaction parameters can be eliminated due to the saturation solubilities in the two pure solvents, $(\chi_A^{sat})_B$ and $(\chi_A^{sat})_C$.

$$RT \ln[a_A^{solid}/(\chi_A^{sat})_B] = a_0^{(AB)} + a_2^{(AB)} \qquad \text{Equation 2.65}$$

$$RT \ln[a_A^{solid}/(\chi_A^{sat})_C] = a_0^{(AC)} + a_2^{(AC)} \qquad \text{Equation 2.66}$$

First, eqs 2.63 and 2.64 are substituted into eq 2.60. Then, it is rearranged algebraically. This allows the solute solubility in binary solvent mixtures to be expressed as a simple

mole fraction average of the measured solute properties in both pure solvents, minus a term involving a power series expansion in solvent composition

$$RT \ln \chi_A^{sat} = \chi_B^0 RT \ln(\chi_A^{sat})_B + \chi_C^0 RT \ln(\chi_A^{sat})_C - \chi_B^0 \chi_C^0 [P_0 + P_1 \chi_B^0 + P_2 \chi_B^{02} + P_3 \chi_B^{03}]$$

Equation 2.67

where $P_0 = a_2^{(AB)} + 3a_2^{(AC)} + a_0^{(BC)} + 4a_2^{(BC)}$

$P_1 = a_2^{(AB)} - 3a_2^{(AC)} - 124a_2^{(BC)}$

$P_2 = a_2^{(AB)} + a_2^{(AC)} + 12a_2^{(BC)}$

and $P_3 = a_1^{(BC)} - 4a_2^{(BC)}$

This power series expansion is third-order in χ_0^B. It can be transformed easily into the Redlich–Kister form. The final derived equation becomes

$$RT \ln \chi_A^{sat} = \chi_B^0 RT \ln (\chi_A^{sat})_B + \chi_C^0 RT \ln (\chi_A^{sat})_C + \chi_B^0 \chi_C^0 \Sigma S_i (\chi_B^0 - \chi_C^0)^i$$

Equation 2.68

the Combined NIBS/Redlich–Kister expression.[36,37,39] The S_i parameters are viewed as simply "curve-fit" numerical values determined by the least-squares analysis of solubility data.

Thus far, the Combined NIBS/Redlich–Kister model has been shown to be a very accurate mathematical representation for how the solubility varies with binary solvent composition. Anthracene and pyrene solubilities have been described successfully with less than 1% deviation from experimental measurements in over two hundred different binary solvent systems using eq 2.68.[40-58] In addition, eq 2.68 has predicted the solubilities of several classes of structurally related drugs in aqueous-organic solvent

mixtures successfully.[59-62] In these latter studies, the Combined NIBS/Redlich–Kister model was written in terms of its volume fraction equivalent

$$\ln \chi_A^{sat} = \phi_B^0 \ln(\chi_A^{sat})_B + \phi_C^0 \ln(\chi_A^{sat})_C + \phi_B^0 \phi_C^0 \Sigma S_i(\phi_B^0 - \phi_C^0)^i$$

Equation 2.69

because the actual experimental data was reported in the literature in terms of mole fraction solubilities of drug molecules measured at a specified binary volume fraction composition. Pharmaceutical chemists often prepare solvent mixtures volumetrically rather than by mass. To derive eq 2.69 from the general NIBS mixing model, simply approximate the weighting factors with molar volumes ($\Gamma_i = V_i$). The weighted mole fractions then become equal to volume fractions.

Once curve-fit parameters are known, most solution models are able to reproduce the experimental solubility data and predict the solute solubility at other binary solvent compositions by interpolation and/or extrapolation methods. Few models can make an outright prediction. Jouyban–Gharamaleki and Acree[60] have shown that it is possible to calculate the solubility of structurally related drugs in water cosolvent mixtures using the Combined NIBS/Redlich–Kister equation. They were able to determine one set of numerical values for the S_i coefficients from one set of drug molecules. Those coefficients then were utilized to predict the solubility behavior of a second set of structurally similar drug molecules not used in the original regression analysis. For benzoate derivatives dissolved in a propylene glycol-water mixture and sulfonamides dissolved in dioxane-water mixtures, the mean percent error in the predicted solubilities was 17.6%.

Recently, the Combined NIBS/Redlich–Kister equation has been extended to describe isothermal solubility data in ternary solvent mixtures.[63-75] Equation 2.68 expresses the logarithmic mole fraction solubility relative to the simple $\chi_B^\circ \ln (\chi_A^{sat})_B + \chi_C^\circ \ln (\chi_A^{sat})_C$ arithmetic average in terms of the Redlich–Kister equation. For a ternary solvent system with components B, C, and D, and solute A, the mathematical representation of the logarithmic mole fraction solubility takes the form of

$$\ln \chi_A^{sat} = \chi_B^\circ \ln(\chi_A^{sat})_B + \chi_C^\circ \ln(\chi_A^{sat})_C + \chi_D^\circ \ln(\chi_A^{sat})_D + \chi_B^\circ\chi_C^\circ \Sigma S_{i,BC}(\chi_B^\circ - \chi_C^\circ)^i + \chi_B^\circ\chi_D^\circ \Sigma S_{j,BD} (\chi_B^\circ - \chi_D^\circ)^j + \chi_C^\circ\chi_D^\circ \Sigma S_{k,CD}(\chi_C^\circ - \chi_D^\circ)^k$$

Equation 2.70

Equation 2.70 can be traced back to 1981, when Acree and Bertrand used the NIBS model to estimate the solubility of benzoic and m-toluic acids in ternary solvent mixtures.[27] They derived expressions based on the assumption that carboxylic acid solutes entirely exist in solution as monomers or dimers. These assumptions represented the two limiting conditions. For molecules that have identical molar volumes, the predictive expression can be written as

$$\ln \chi_A^{sat} = \chi_B^\circ \ln(\chi_A^{sat})_B + \chi_C^\circ \ln(\chi_A^{sat})_C + \chi_D^\circ \ln(\chi_A^{sat})_D + \Delta G_{BCD}^E (RT)^{-1}$$

Equation 2.71

a mole fraction average of the logarithmic solute solubilities in the three pure solvents, plus a term containing the excess Gibbs energy of the ternary solvent mixture. Equation 2.71 is applicable only for solutes having very limited saturation solubilities.

In the early days of ternary solvent mixture research, the thermodynamic properties were scarce. Acree and Bertrand had to estimate the required ΔG_{BCD}^E values

from available binary vapor-liquid equilibria (VLE) data. Equation 2.70 can be derived by substituting the Redlich–Kister prediction for

$$\Delta G^{E}_{BCD} = \chi_B^\circ \chi_C^\circ \Sigma\, G_{i,BC}(\chi_B^\circ - \chi_C^\circ)^i + \chi_B^\circ \chi_D^\circ \Sigma\, G_{i,BD}(\chi_B^\circ - \chi_D^\circ)^j + \chi_C^\circ \chi_D^\circ \Sigma\, G_{k,CD}(\chi_C^\circ - \chi_D^\circ)^k \qquad \text{Equation 2.72}$$

into eq 2.71. The various $G_{i,BC}$, $G_{j,BD}$, and $G_{k,CD}$ values represent coefficients deduced from a regressional analysis of binary VLE data. Now that solubilities in binary systems are becoming more available, the Redlich–Kister coefficients are determined now from solute solubilities in three contributing sub-binary solvent mixtures rather than VLE data. To indicate this practice, the various curve-fit coefficients in eq 2.70 are denoted as $S_{i,BC}$, $S_{j,BD}$, and $S_{k,CD}$.

Deng thoroughly discussed the predictive abilities of the Combined NIBS/Redlich–Kister for 34 ternary solvent systems consisting of: (1) an alkoxyalcohol, an alkane, and an alkane; (2) an alcohol, an alkane, and an alkane; (3) an alcohol, an alcohol, and an alkane; (4) an alcohol, an alkoxyalcohol, and an alkane; and (5) an alcohol, an alcohol, and an alkoxyalcohol.[63] Deng concluded that the Combined NIBS/Redlich–Kister model predicted the solubility behavior of anthracene with an overall absolute average deviation of 1.39%. This is slightly less than experimental uncertainty associated with each measured mole fraction solubility. There is no reason to believe that this model could not be applied to other solutes and solvent systems. However, one does need to assess carefully the model's predictive ability by using systems that cover a much wider range of saturation mole fraction solubilities. The

ternary solvent systems studied by Deng[63] covered approximately a four-fold range in anthracene mole fraction solubility.

As an informational note for mixed solvent systems, the observed mole fraction solubility of a dissolved solute generally falls somewhere between the mole fraction solubilities measured in the pure solvents. Many solution models are able to predict with reasonable accuracy solubility in solvent systems that cover very small ranges in mole fraction solubilities and in solvent mixtures that contain very similar solvent components (i.e. all alkane solvents, all alcohol solvents). A more demanding test of a model's predictive ability is to predict solubilities that cover very large ranges in solute mole fraction solubilities. For this reason, anthracene solubilities were measured in 47 ternary ether + alcohol + hydrocarbon solvent systems. These latter systems contain three dissimilar types of solvent molecules. They are believed to involve the formation of hydrogen-bonds (e.g. alcohol self-association and formation of ether-alcohol complexes) and should exhibit greater solution nonideality than the systems studied by Deng.[63] Moreover, the ether + alcohol + alkane solvent systems cover a much wider 20-fold range in anthracene solubility. Establishing the predictive ability of the Combined NIBS/Redlich–Kister equations is important in that Acree and coworkers now have generated a relatively extensive solubility database for pyrene, benzil, trans-stilbene, carbazole, thianthrene and anthracene dissolved in over 250 binary solvent systems. The Combined NIBS/Redlich–Kister equation allows one to predict pyrene, benzil, trans-stilbene, etc. solubilities in every ternary solvent combination from which all sub-binary solvent solubility data exists. The Combined NIBS/Redlich–Kister model is preferred by

many research groups, because of its simplicity and availability for calculation by common software and scientific hand calculators. Previously, it was demonstrated that its application can be expanded to the prediction of solubility in different temperatures and the solubility of structurally related solutes in mixed solvents. Without the Combined NIBS/Redlich– Kister model, however, it would take several years to measure the solubility of a large number of ternary solvent mixtures that can now be calculated in a matter of minutes.

Kretschmer–Wiebe Association Model

The thermodynamic solution models discussed thus far do not really contain provisions for complexation. There are no equilibrium and/or association constants in the final derived equations. While it may be possible to predict and to mathematically describe experimental anthracene solubility data in ternary solvent mixtures containing hydrogen-bonding alcoholic cosolvents with the Combined NIBS/Redlich–Kister model, it must be remembered that the curve-fit coefficients are strictly empirical in nature. The coefficients are reduced by regressing actual experimental data in accordance with eq 2.61. There is absolutely no correlation between the numerical values of the S_i curve-fit parameters and the molecular structures of the dissolved solute and various solvent molecules.

There are several reasons for developing and using models. Engineers use thermodynamic models to predict desired quantities whenever actual experimental values are not available in the chemical literature. Chemists, on the other hand, use

thermodynamic models to obtain a better understanding of molecular interactions in solution and to calculate meaningful association constants, whose numerical values can be confirmed by several independent experimental methods. In the case of alcohol-hydrocarbon mixtures, there have been two classical treatments that have appeared in the chemical literature. The first treatment to be discussed is the Kretschmer–Wiebe model. For a ternary solution containing an alcohol (component A) and two inert hydrocarbons (components B and C), the Kretschmer–Wiebe model[76] assumes that the excess Gibbs energy, ΔG_{ABC}^{E}, is described by the sum of two separate contributions:

$$\Delta G_{ABC}^{E} = (\Delta G_{ABC}^{E})_{ph} + (\Delta G_{ABC}^{E})_{ch} \qquad \text{Equation 2.73}$$

One contribution represents chemical interactions; the other represents physical interactions. The chemical contribution was put in the form of a step-wise, self-association model. It basically assumes that the alcohol forms continuous linear hydrogen-bonded polymers $C_1, C_2, C_3, \ldots, C_i, \ldots$ by successive chemical reactions

$$C_1 + C_1 \rightleftharpoons C_2$$

$$C_2 + C_1 \rightleftharpoons C_3$$

•

•

•

$$C_i + C_1 \rightleftharpoons C_{i+1}$$

•

described by a single isodesmic equilibrium constant of the form [76]

$$K_A = \hat{C}_{Ai+1}/\hat{C}_{Ai}\hat{C}_{A1}V_A = [\hat{\phi}_{Ai+1}/\hat{\phi}_{Ai}\hat{\phi}_{A1}][i/(i+1)] \qquad \text{Equation 2.74}$$

where $\hat{C}_{Ai}$ and $\hat{\phi}_{Ai}$ refer to the molar concentration and volume fraction of the *i*-mer, respectively. At a fixed temperature, K_A, depends only on the alcohol and is independent of the other molecules in the mixture. An isodesmic equilibrium constant is defined as having identical numerical values for each consecutive, stepwise association. The volume fraction of the i-mer is calculated by using the molar volume of the monomer multiplied by *i*. The inclusion of cyclic polymers into the model increases the complexity of the derived expressions well beyond the scope of this dissertation. Thus, they will not be considered.

From eq 2.74, the concentration of an individual alcohol *i*-mer can be expressed as

$$\hat{C}_{Ai} = \hat{n}_{Ai}/V = \hat{C}_{Ai-1}\hat{C}_{A1}K_AV_A = \hat{C}_{A1}(K_A\hat{C}_{A1})^{i-1} \qquad \text{Equation 2.75}$$

The stoichiometric volume fraction of the alcohol, ϕ_A, is the sum of the volume fractions of each individual alcohol species

$$\phi_A = \Sigma\, \hat{\phi}_{Ai} = (1/K_A)\, \Sigma\, i(K_A\hat{\phi}_{A1})^i = \hat{\phi}_{A1}(1 - K_A\hat{\phi}_{A1})^{-2}$$

Equation 2.76

for this infinite series to converge, $|K_A\phi_{A1}| < 1$. The volume fraction of the alcohol monomer in the ternary solution is

$$\hat{\phi}_{A1} = [(2K_A\phi_A + 1) - (1 + 4K_A\phi_A)^{1/2}]/(2K_A^2\phi_A) \qquad \text{Equation 2.77}$$

obtained by solving eq 2.76.

The chemical part of the Gibbs energy is based on the Flory–Huggins athermal model and may be written as

$$(g^{m}_{ABC})_{ch} = RT\,[\Sigma\, n\hat{}_{Ai} \ln \phi\hat{}_{Ai} + n\hat{}_{B} \ln \phi\hat{}_{B} + n\hat{}_{C} \ln \phi\hat{}_{C}]$$

Equation 2.78

Through differentiation and suitable mathematical manipulations, the expression for $(\Delta G_{ABC}{}^{E})_{ch}$ can be derived.

$$(\Delta G_{ABC}{}^{E})_{ch} = RT[\chi_{A} \ln(\phi\hat{}_{A1}/\phi\hat{}_{A1}{}^{*}\chi_{A}) + \chi_{B} \ln(\phi_{B}/\chi_{B}) + \chi_{C} \ln(\phi_{C}/\chi_{C}) + \chi_{A}K_{A}(\phi\hat{}_{A1} - \phi\hat{}_{A1}{}^{*})]$$

Equation 2.79

The simplest equation that adequately might describe the physical contribution to the excess Gibbs energy $(\Delta G_{ABC}{}^{E})_{ph}$ of a ternary alcohol plus two inert hydrocarbon system is

$$(\Delta G_{ABC}{}^{E})_{ph} = (n_{B}V_{B} + n_{C}V_{C} + \Sigma\, n\hat{}_{Ai}V_{Ai})^{-1} \times$$

$$[n_{B}V_{B}n_{C}V_{C}A_{BC} + \Sigma\, n_{Ai}V_{Ai}n_{Bi}V_{Bi}A_{AiB} + \Sigma\, n\hat{}_{Ai}V_{Ai}n_{C}V_{C}A_{AiC}]$$

Equation 2.80

in which the A_{ij} terms represent binary interaction parameters. Equation 2.80 is not very useful because there are too many parameters. However, reasonable assumptions allow the number of parameters to be reduced significantly. The previously mentioned solubility parameter approach of Scatchard–Hildebrand gives a basis for estimation of interaction parameters involving alcohol complexes

$$A_{AiK} = (\delta_{Ai} - \delta_{K})^{2}\,, \qquad K = B, C \qquad \text{Equation 2.81}$$

If we make the assumption that the solubility parameter of an alcohol polymer (δ_{Ai+1}) is a weighted molar volume average of the solubility parameters of the *i*-mer and monomer

$$\delta_{Ai+1} = (V_{Ai}\delta_{Ai} + V_{A1}\delta_{A1})/(V_{Ai} + V_{A1}) = (i\delta_{Ai} + \delta_{A1})/(i + 1) = \delta_{Ai}$$

Equation 2.82

gives

$$A_{AiB} = A_{A1B} \quad \text{and} \quad \mathbf{A}_{AiC} = A_{A1C}$$ Equation 2.83

The combination of eqs 2.80–2.83 enables $(\Delta G_{ABC}^{E})_{ph}$ to be expressed

$$(\Delta G_{ABC}^{E})_{ph} = (n_A V_A + n_B V_B + n_C V_C)^{-1}[n_A V_A n_B V_B A_{A1B} + n_A V_A n_C V_C A_{A1C} + n_B V_B n_C V_C A_{BC}]$$

Equation 2.84

in terms of three binary interaction parameters. If we substitute eqs 2.79 and 2.84 into eq 2.74, we arrive at the following expressing for the total Gibbs energy of the ternary system (per stoichiometric mole of solution)

$$(\Delta G_{ABC}^{E}) = RT[\chi_A \ln(\hat{\phi}_{A1}/\hat{\phi}_{A1}^{*}\chi_A) + \chi_B \ln(\phi_B/\chi_B) + \chi_C \ln(\phi_C/\chi_C) + \chi_A K_A(\hat{\phi}_{A1} - \hat{\phi}_{A1}^{*})] + (\chi_A V_A + \chi_B V_B + \chi_C V_C)[\phi_A\phi_B A_{A1B} + \phi_A\phi_C A_{A1C} + \phi_B\phi_C A_{BC}]$$

Equation 2.85

The corresponding expression for the excess enthalpy of mixing can be obtained from the standard thermodynamic relationship

$$\Delta H^{E} = \partial(\Delta G^{E}/T) / \partial(1/T)$$ Equation 2.86

once we have an expression for the excess Gibbs energy. In the majority of published applications the standard enthalpy of formation of an alcohol-alcohol hydrogen bond (assumed to be independent of the degree of imerization) was set equal to – 25 kJ mol^{-1}.

Thermodynamic principles relate solubility to chemical potential. For a system obeying eq 2.85, the solubility of a sparingly soluble solute ($\phi_A^{sat} = 0$) is

$$RT \ln a_A^{solid} = RT\{\ln \phi_A^{sat} + \phi_B^{\circ}(1 - V_A/V_B) + \phi_C^{\circ}[1 - (V_A/V_C)(1 - K_C\phi_{C1})]\} +$$

$$V_A[\phi_B^{\circ}A_{AB} + \phi_C^{\circ}A_{AC1} - \phi_B^{\circ}\phi_C^{\circ}A_{BC1}] \qquad \text{Equation 2.87}$$

obtained by differentiating ΔG_{ABC} with respect to the number of moles of solute. For consistency, the identity of the chemicals is going to be changed back to where component A denotes the solute, and where components B and C refer to the inert hydrocarbon and alcohol solvents, respectively. Careful examination of eq 2.87 reveals that the A_{AB} and A_{AC1} parameters can be eliminated from the basic model via

$$RT \ln a_A^{solid} = RT[\ln(\phi_A^{sat})_B + 1 - (V_A/V_B)] + V_A A_{AB}$$

Equation 2.88

and

$$RT \ln a_A^{solid} = RT[\ln(\phi_A^{sat})_C + 1 - (V_A/V_C)(1 - K_C\hat{\phi}_{C1}^{*})] + V_A A_{AC1}$$

Equation 2.89

where $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$ denote the volume fraction solubilities in the two pure solvents. Through performing these substitutions, one obtains a relatively simple mathematical expression for the solubility of a solute dissolved in binary hydrocarbon + alcohol solvent mixtures:

$$\ln a_A^{solid} = \phi_B^{\circ} \ln(\phi_A^{sat})_B + \phi_C^{\circ} \ln(\phi_A^{sat})_C - \phi_C^{\circ}(V_A/V_C)K_C(\hat{\phi}_{C1} - \hat{\phi}_{C1}^{*}) +$$

$$V_A\phi_B^{\circ}\phi_C^{\circ}(\delta_B' - \delta_C')^2(RT)^{-1} \qquad \text{Equation 2.90}$$

which does not require a prior knowledge of the enthalpy of fusion and melting point temperature of the solute. Elimination of the a_A^{solid} term from the predictive equation can lead to better solubility estimates, particularly in the case of high melting point solutes such as anthracene. Two additional terms involving differences between the molar heat capacities of the liquid and solid, ΔC_p, would have to be dropped from the more rigorous a_A^{solid} computation[3] (see eq 2.17) as ΔC_p data for anthracene is not available in the chemical literature. Finally, the derived expression correctly describes the solubility in both pure self-associating solvents. Also, it can be used to calculate the "optimum values" of the self-association constant of the alcohol solvent from measured solubility as a function of solvent composition.

Despite the complex appearance of eq. 2.90, its application to solubilities in mixed solvents is relatively straightforward and is similar in concept to numerical examples presented previously.[77] The quantities $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$ are calculated from the measured mole fraction solubility of the solid in the pure solvents. The assumption is that the excess molar volumes, modified solubility parameters, and an assumed value for the equilibrium constant are used then in eq 2.90 to calculate ϕ_A^{sat} at each binary solvent composition. If one so chose, the entire procedure could be repeated until the numerical value of K_C that "best" describes the experimental solubility in a particular binary solvent system is obtained. One perhaps could adjust the numerical value of $\delta'_{alcohol}$ in the hope of improving the descriptive accuracy. If used in this manner, eq 2.90 is a simple mathematical representation.

Alternatively, the equation can be used to make outright solubility predictions by inserting numerical values of K_C and modified solubility parameters deduced from nonsolubility measurements. Nagata[78] has calculated "best" K_C values for several of the more common alcohols by regressing vapor-liquid equilibria data and excess enthalpy of mixing data for binary hydrocarbon + alcohol mixtures. As might be surmised, the model does not describe perfectly the experimental data. For each alcohol, the K_C value that was reported represented the so-called "best" value that minimized deviations between the experimental and calculated Gibbs energy and excess enthalpy data for the given alcohol with several different saturated hydrocarbons. If the K_C values of Nagata are used, then eq 2.90 is a predictive expression.

Acree and Tucker[79] examined the two K_C terms in detail for 30 binary alkane + alcohol solvent mixtures. They compared measured anthracene solubilities taken from chemical literature[80,81] and predicted values based upon eq 2.90 using the alcohol self-association constants taken from the work of Nagata. The modified solubility parameters that were used accounted only for nonspecific interactions, thus removing the case of hydrogen-bonding contributions for the alcohols. The modified solubility parameters were taken from tabulated values given in the chemical literature.[12,82-97] They showed that the Kretschmer–Wiebe model provides reasonably accurate predictions of the solubility behavior of anthracene in the rather nonideal alcohol solvents. Generally speaking, the deviations are on the order of approximately ± 8% or less, which is probably the best one could hope for based upon the large number of assumptions that went into deriving the final predictive expression. Predictions could not be made for all

of the existing anthracene solubility data, because numerical values of K_C were not available for several alcohols. This was particularly true for many of the larger, nonvolatile alcohols, like 2-ethyl-1-hexanol. To date, the Kretschmer–Wiebe model has not been used to predict solubilities in ternary solvent mixtures. The authors also looked at the value of K_C that optimized the prediction, and thus, reduced the average absolute deviation. They could not state definitively why the optimized K_C values were much less than Nagata's values, or why for any given alcohol the K_C value varied with the inert hydrocarbon cosolvent. They, however, did note that molecular interactions in these systems are undoubtedly more complex than those incorporated into this particular version of the Kretschmer–Wiebe theory. Therefore, they viewed Kretschmer–Wiebe theory as providing a very reasonable (although by no means perfect) thermodynamic description of anthracene dissolved in binary alkane + alcohol mixtures.

The authors perhaps could have improved the predictive accuracy of the Kretschmer–Wiebe model by assuming a different mathematical description of nonspecific interactions. Nagata has used the Kretschmer–Wiebe model a number of times successfully to describe and predict vapor-liquid and liquid-liquid equilibria and excess enthalpies of both binary and ternary mixtures containing a single alcohol and two saturated hydrocarbons. In the very early applications, nonspecific interactions were described in terms of the Scatchard–Hildebrand solubility parameter model, as was the case in the Acree and Tucker study. Nagata[98] later proposed a more sophisticated description of nonspecific interactions that took the mathematical form of

$$(\Delta G_{ABC}^{E})_{phys} = -\Sigma\, \chi_i \ln(\Sigma\, \phi_j \tau_{ji}) \qquad \text{Equation 2.91}$$

and

$$(\Delta H_{ABC}^{E})_{ph} = \Sigma\, \chi_i [\, \Sigma\, \phi_j (\partial \tau_{ji} / \partial (1/T)) / \Sigma\, \phi_j \tau_{ji}] \qquad \text{Equation 2.92}$$

where

$$\tau_{ji} = \exp[-(u_{ij} - u_{jj})/RT]$$

for $(\Delta G_{ABC}^{E})_{ph}$ and $(\Delta H_{ABC}^{E})_{ph}$ of ternary alcohol plus two hydrocarbon mixtures. From a practical standpoint, using two coefficients per binary solution provides a better mathematical representation of the experimental data. Numerical values of the two binary mixture coefficients were determined by regressing the experimental vapor-liquid and liquid-liquid equilibrium data, or excess enthalpy data, in accordance with the model's final derived equations. For each binary mixture, the author had several experimental data points, and the regression was not a problem. For applications involving solubility, this is not the case. One has only a single experimental saturation mole fraction solubility for each solute-solvent binary pair. It is not possible mathematically to calculate two binary mixture coefficients from only a single measured value. That would be solving one mathematical equation with two unknowns.

Historically, the Kretschmer–Wiebe model was proposed many years before computerized calculations became so common. As a result, it often was necessary to make simplifying approximations in order to arrive at a mathematical equation that could be solved with the existing technology. In retrospect, many of the approximations made were totally unrealistic, given the functional groups and molecules involved. An early extension of the Kretschmer–Wiebe model to ternary systems containing a saturated hydrocarbon and two different alcohol molecules treated the mixture as a "pseudobinary"

system. The two alcohols were treated as a single alcohol. Their association constant, molar volume, and modified solubility parameter varied with composition. This particular treatment allowed researchers to use exactly the same mathematical equations that had been derived for binary alkane + alcohol mixtures. The only requirement on the properties of the "pseudoalcohol" were that they must go to properties of the pure alcohols in the absence of the second alcohol. The molar volume of the "pseudoalcohol" was assumed to be a mole fraction average of the molar volumes of pure alcohols B and C (i.e., $V_{alcohol} = \chi_B{}^\circ V_B + \chi_C{}^\circ V_C$). The modified solubility parameter of the "pseudoalcohol" was taken to be a volume fraction average of the modified solubility parameters of the two pure alcohols (i.e., $\delta_{alcohol} = \phi_B{}^\circ \delta_B' + \phi_C{}^\circ \delta_C'$). The molar volume approximation corresponds to that of an ideal solution. This seems reasonable, given the fact that binary alcohol + alcohol mixtures rarely exhibit large deviations from ideality. The approximation concerning the $\delta'_{alcohol}$ is consistent with how one defines the solubility parameter of a binary solvent (see eq 2.21).

For molar volumes and modified solubility parameters, there was an existing precedent for defining the values of a "pseudoalcohol." This was not the case, however, for the association constant. Nagata,[99] in his study of excess enthalpies of ternary alkane + alcohol + alcohol mixtures, examined the effect of estimating K by four different methods:

$$K_{avg} = K_B\chi_B{}^2 + 2K_B{}^{1/2}K_C{}^{1/2} + K_C\chi_C{}^2$$

$$K_{avg} = K_B\chi_B + K_C\chi_C$$

$$K_{avg} = K_B\chi_B{}^2 + 2\chi_B\chi_C/(\chi_B/K_B + \chi_C/K_C) + K_C\chi_C{}^2$$

$$1/K_{avg} = 1/(\chi_B/K_B + \chi_C/K_C)$$

Careful examination of the summarized computations presented in the Nagata paper indicates that while several of the approximations may provide reasonable estimations, there is no a priori means for determining which approximation will be best for any given ternary system.

Pando et al.[100,101] employed a completely different approach in the thermodynamic treatment of binary mixtures containing two alcohols. Each alcohol molecule was permitted to self-associate in stepwise fashion

$$B_1 + B_1 \rightleftharpoons B_2$$

$$B_2 + B_1 \rightleftharpoons B_3$$

• • •

• • •

$$B_i + B_1 \rightleftharpoons B_{i+1}$$

• • •

• • •

and

$$C_1 + C_1 \rightleftharpoons C_2$$

$$C_2 + C_1 \rightleftharpoons C_3$$

• • •

• • •

$$C_i + C_1 \rightleftharpoons C_{i+1}$$

• • •

• • •

Two isodesmic equilibrium constants

$$K_B = \hat{C}_{Bi+1} / \hat{C}_{Bi}\hat{C}_{B1}V_B = [\hat{\phi}_{Bi+1} / \hat{\phi}_{Bi}\hat{\phi}_{B1}][i /(i + 1)]$$

$$K_C = \hat{C}_{Ci+1} / \hat{C}_{Ci}\hat{C}_{C1}V_C = [\hat{\phi}_{Ci+1} / \hat{\phi}_{Ci}\hat{\phi}_{C1}][i /(i + 1)]$$

governed the formation of all polymeric association complexes. Hydrogen bonding between dissimilar alcohol molecules was forbidden. The above assumptions introduced one additional term, $RT\chi_B K_B(\hat{\phi}_{B1} - \hat{\phi}_{B1}^*)$, into the chemical contribution portion of the Gibbs energy of mixing terms. The final derived equation

$$\Delta G_{BC}^E = RT[\chi_B \ln(\hat{\phi}_{B1} / \hat{\phi}_{B1}^* \chi_B) + \chi_C \ln(\hat{\phi}_{C1} / \hat{\phi}_{C1}^* \chi_C) + \chi_B K_B(\hat{\phi}_{B1} - \hat{\phi}_{B1}^*) + \chi_C K_C(\hat{\phi}_{C1} - \hat{\phi}_{C1}^*)] + (\chi_B V_B + \chi_C V_C)[\phi_B \phi_C A_{B1C1}] \quad \text{Equation 2.93}$$

and the corresponding excess enthalpy of mixing expression were found to provide reasonably accurate predictions of the observed vapor-liquid equilibria (VLE) and measured excess enthalpies of 21 binary alcohol + alcohol systems. These findings occurred despite the fact that the model neglected cross-associations.

Nagata and Gotoh[102] provided perhaps the most realistic treatment by including provisions for cross-association:

$$B_i + C_j \rightleftharpoons B_i C_j$$

$$B_j + C_i \rightleftharpoons B_jC_i$$

$$B_iC_j + B_k \rightleftharpoons B_iC_jB_k$$

$$B_iC_jB_k + C_l \rightleftharpoons B_iC_jB_kC_l$$

The equilibrium constant for these reactions is K_{BC}. The additional equilibria lead to very complex mathematical expressions for the mass balance constraints on the stoichiometric volume fractions of the two alcohol molecules

$$\phi_B = S_B + (V_BK_{BC}S_BS_C^*)[2 + V_CK_{BC}S_B^*(2 - V_BV_CK_{BC}^2S_B^*S_C^*) + V_BK_{AB}S_C^*] / (1 - V_BV_CK_B^2S_B^*S_C)^2 \qquad \text{Equation 2.94}$$

and

$$\phi_C = S_C + (V_CK_{BC}S_B^*S_C)[2 + V_BK_{AB}S_C^*(2 - V_BV_CK_{AB}^2S_B^*S_C^*) + V_CK_{BC}S_B^*] / (1 - V_BV_CK_{AB}^2S_B^*S_C^*)^2 \qquad \text{Equation 2.95}$$

where

$$S_B = \hat{\phi}_{B1} / (1 - K_B\hat{\phi}_{B1})^2$$

$$S_B^* = \hat{\phi}_{B1} / (1 - K_B\hat{\phi}_{B1})$$

$$S_C = \hat{\phi}_{C1} / (1 - K_C\hat{\phi}_{C1})^2$$

$$S_B^* = \hat{\phi}_{C1} / (1 - K_C\hat{\phi}_{C1})$$

which were extremely difficult to solve with existing computer programs. For years Nagata and Gotoh's work went virtually unnoticed. It was not until Campbell[103] solved the Kretschmer–Wiebe model in closed form for mixtures containing any number of associating species that researchers really began to consider seriously this thermodynamic

model for describing mixtures of two alcohol molecules. The notation used by Campbell differs slightly from that employed by Nagata and Gotoh.

The essential features of the Kretschmer–Wiebe association model, pertaining to a ternary mixture containing an inert solute (component A) and two alcohol cosolvents (components B and C), will be reviewed briefly. This will facilitate development of the final derived predictive expression. The basic model assumes that two alcohols form both continuous homogeneous hydrogen-bonded

$$B_i + B_1 \rightleftharpoons B_{i+1} \qquad K_B = \hat{C}_{Bi+1}/(\hat{C}_{Bi}\hat{C}_{B1})$$

$$C_i + C_1 \rightleftharpoons C_{i+1} \qquad K_C = \hat{C}_{Ci+1}/(\hat{C}_{Ci}\hat{C}_{C1})$$

and heterogeneous hydrogen-bonded polymers

$$C_1 + \text{Polymer} - B \rightleftharpoons \text{Polymer} - B - C \qquad K_{BC} = \hat{C}_{\text{Polymer - B - C}}/(\hat{C}_{C1}\hat{C}_{\text{Polymer - B}})$$

$$B_1 + \text{Polymer} - C \rightleftharpoons \text{Polymer} - C - B \qquad K_{CB} = \hat{C}_{\text{Polymer - C - B}}/(\hat{C}_{B1}\hat{C}_{\text{Polymer - C}})$$

by successive chemical reactions. The isodesmic equilibrium constants, K_B and K_C, describe the formation of homogeneous hydrogen-bonded polymers, B_{i+1} and C_{i+1}, respectively. They are expressed in terms of molar concentrations of the true species in solution. The true species that exist in the associated solution are denoted by the overbar, ($\hat{}$) .

There are two features of the standard Gibbs energy which relate to the heterogeneous hydrogen-bond formation: 1) independence of the composition of the polymeric chain, and 2) dependence on the equilibrium between a chain terminating with

alcohol B and a single alcohol C monomer. This is in agreement with the chemical reaction previously cited for the formation of heterogeneous Polymer–B–C. An additional assumption is that the standard energy change is the same for a single alcohol B monomer in equilibrium with a polymer chain that ends in alcohol C (i.e., $K_{BC} = K_{CB}$). A chemical reaction between a Polymer–B chain and an alcohol B monomer may be described mathematically by the isodesmic equilibrium constant K_B. The range in size of true species exists from the monomers of each stoichiometric component to a linear chain of essentially infinite length composed of any combination of alcohols B and C.

Thermodynamically, the ternary-associated solution can be modeled by either the concentrations for the three stoichiometric components that are calculated, as if self-association did not occur, or by the concentrations of species believed to exist in solution. The volume fraction ϕ_i and molar concentration C_i of stoichiometric species *i* are defined as

$$\phi_i = \chi_i V_i / \Sigma \chi_j V_j = n_i V_i / \Sigma n_i V_i \qquad \text{Equation 2.96}$$

$$C_i = \phi_i / V_i = n_j / \Sigma n_j V_j \qquad \text{Equation 2.97}$$

respectively, where χ_i is the stoichiometric mole fraction, and n_i is the stoichiometric number of molecules of component *i*. The above summation extends over the three components in the solution. The parameter V_i in eqs 2.96 and 2.97 is a measure of molecular size for the stoichiometric species. It is normalized arbitrarily to the molar volume of methanol at 303.15 K ($V_{methanol} = 41.0\ cm^3\ mol^{-1}$) according to $V_i = (V_i/V_{methanol})_{303.15\ K}$. Similarly, the volume fraction and molar concentrations of a true species s are

$$\hat{\phi}_s = \hat{\chi}_s V_s / \Sigma \hat{\chi}_t V_t = \hat{n}_s V_s / \Sigma \hat{n}_t V_t \qquad \text{Equation 2.98}$$

$$\hat{C}_s = \hat{\phi}_s / V_s = \hat{n}_s / \Sigma \hat{n}_t V_t \qquad \text{Equation 2.99}$$

expressed in terms of true mole fractions and mole numbers. The numerical values of the size parameters of the true species are assumed to be additive, and the size parameters of the alcohol monomers are the same as for the corresponding stoichiometric species. For example, the size parameter for true species BCBBC in the ternary mixture would be $V_{BCBBC} = 3V_{B1} + 2V_{C1} = 3V_B + 2V_C$.

The next step is to utilize the counting scheme of Campbell[103] to distinguish between the different true polymeric entries. True species are characterized by two characteristics: 1) the chain length (total number of various alcohol monomers in the chain), and 2) the monomer that is at the terminal position on the chain. The molar concentration of the hydrogen-bonded complex of length *n* that ends in alcohol monomer B will be denoted by $\hat{C}_{B,n}$. Similarly, $\hat{C}_{C,n}$ denotes the chain ending with alcohol cosolvent C. As examples of the notations, C_B and C_C are the overall stoichiometric concentrations of alcohols B and C, respectively. $\hat{C}_{B,1}$ is the molar concentration of alcohol B monomer. $\hat{C}_{B,4}$ is the molar concentration of hydrogen-bonded polymers having chains that are four molecules in length and with alcohol B as the terminal group.

The true alcohol species concentrations are expressed by both the terms of the monomer group that ends the chain and the terms of the total chain length. The total concentration of complexes is given by

$$\Psi_{Total} = \hat{C}_A + \hat{C}_{B,1} + \hat{C}_{B,2} + \hat{C}_{B,3} + \ldots + \hat{C}_{C,1} + \hat{C}_{C,2} + \hat{C}_{C,3} + \ldots$$

Equation 2.100

For a binary mixture containing two alcohols, eq 2.100 can be reduced to the following closed mathematical form[103]

$$\Psi_{Total} = C_A + \Psi_B + \Psi_C \qquad \text{Equation 2.101}$$

where Ψ_B and Ψ_C are obtained from simultaneous (iterative) solution of

$$\Psi_B = C_B/(1 + K_B\Psi_B + K_{BC}\Psi_C) \qquad \text{Equation 2.102}$$

$$\Psi_C = C_C/(1 + K_{BC}\Psi_B + K_C\Psi_C) \qquad \text{Equation 2.103}$$

Computation requires a prior knowledge of both homogeneous self-association constants (K_B and K_C) and the single cross-association constant (K_{BC}). This latter quantity has been approximated[103,104] as a simple geometric average of K_B and K_C (i.e., $K_{BC} = (K_BK_C)^{1/2}$) in binary alcohol-alcohol liquid-vapor equilibrium studies.

An understanding of the essential features and notation of the Kretschmer–Wiebe model provides a foundation for the development of a predictive expression for solute solubility in binary solvent mixtures containing two alcohol cosolvents. A description of the Gibbs energy of mixing (relative to the pure liquids) is the sum of two separate contributions, either chemical or physical interactions. The chemical contribution based upon the Kretschmer–Wiebe model discussed above is

$$(\Delta G_{ABC})_{chem} = RT[n_A \ln \phi_A + n_B \ln(\hat{C}_{B,1}/ \hat{C}_{B,1}^{*}) + n_C \ln(\hat{C}_{C,1}/ \hat{C}_{C,1}^{*}) + n_A(1 - \phi_A) +$$

$$n_BV_BC_A + n_CV_CC_A - (n_AV_A + n_BV_B + n_CV_C)(\Psi_B + \Psi_C) + n_B\Psi_B^{*} + n_C\Psi_C^{*}]$$

Equation 2.104

It is written in terms of stoichiometric concentrations wherever possible. Quantities

$\hat{C}_{B(\text{or } C),1}$ and $\hat{C}_{B(\text{or } C),1}^{*}$ refer to both the molar concentrations of the monomers in the mixture and in the neat alcohols, respectively. Numerical values of $\Psi_{B(\text{or } C)}^{*}$ and $\hat{C}_{B(\text{or } C),1}^{*}$ for the two pure alcohols are obtained through application of eqs 2.102 and 2.103 and $\hat{C}_{B(\text{or } C),1} = \Psi_{B(\text{or } C)}^{2}/C_{B(\text{or } C)}$. In the neat alcohols, $C_{B(\text{or } C)}$ is simply the reciprocal of $V_{B(\text{or } C)}$, and $\Psi_{B(\text{or } C)}$. They are the only non-zero values of Ψ_i. These simplifications result in a set of equations

$$1/V_{B(\text{or } C)} = \hat{C}_{B(\text{or } C),1}^{*}/(1 - K_{B(\text{or } C)}\hat{C}_{B(\text{or } C),1}^{*})^2 \qquad \text{Equation 2.105}$$

$$\Psi_{B(\text{or } C)}^{*} = \hat{C}_{B(\text{or } C),1}^{*}/(1 - K_{B(\text{or } C)}\hat{C}_{B(\text{or } C),1}^{*}) \qquad \text{Equation 2.106}$$

that can be solved for $\hat{C}_{B(\text{or } C),1}^{*}$ and $\Psi_{B(\text{or } C)}^{*}$.

Physical effects are expressed in terms of the Nearly Ideal Binary Solvent (NIBS) model developed by Bertrand and coworkers[25,26]

$$(\Delta G_{ABC})_{phys} = (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)^{-1} \times (n_A\Gamma_A n_B\Gamma_B\beta_{AB} + n_A\Gamma_A n_C\Gamma_C\beta_{AC} + n_B\Gamma_B n_C\Gamma_C\beta_{BC}) \qquad \text{Equation 2.107}$$

where Γ_i is the weighting factor for component *i*, and β_{ij} is a binary interaction parameter that is independent of composition. The NIBS model provides[40] reasonably accurate predictions for naphthalene, iodine, *p*-benzoquinone, anthracene, pyrene, and carbazole solubilities in systems containing only nonspecific interactions. Precise applicability of eq 2.107 to Gibbs energy and its temperature and pressure derivatives requires that weighting factors be independent of both variables. Therefore, molar volumes and experimentally determined weighting factors must be regarded as approximations of these true weighting factors. Applications to the conditions of varying temperature

and/or pressure, molar volumes and weighting factors should be referred to as a specific condition, such as 303.15 K and 1 atm or to an extrapolated state, such as a "close-packed" volume. For our applications, weighting factors will be approximated by the stoichiometric size parameter V_i.

Combination of eqs 2.104 and 2.107 yields the following expression for the total Gibbs energy of mixing of the ternary system (per stoichiometric mole of solution)

$$\Delta G_{ABC} = RT[n_A \ln \phi_A + n_B \ln(\hat{C}_{B,l}/ \hat{C}_{B,l}^{*}) + n_C \ln(\hat{C}_{C,l}/ \hat{C}_{C,l}^{*}) + n_A(1 - \phi_A) + n_B V_B C_A + n_C V_C C_A - (n_A V_A + n_B V_B + n_C V_C)(\Psi_B + \Psi_C) + n_B \Psi_B^{*} + n_C \Psi_C^{*}] + (n_A V_A + n_B V_B + n_C V_C)^{-1} \times (n_A V_A n_B V_B \beta_{AB} + n_A V_A n_C V_C \beta_{AC} + n_B V_B n_C V_C \beta_{BC})$$

Equation 2.108

when weighting factors are replaced with the molecular size parameters, V_i. Thermodynamic principles relate solubility to chemical potential. For a system obeying eq 2.108, the volume fraction solubility of a crystalline solute A in alcohols B and C is

$$RT \ln \phi_A^{sat} = RT[\ln a_A^{solid} - (1 - \phi_A^{sat}) + V_A(\Psi_B + \Psi_C)] - V_A[\phi_B^2 \beta_{AB} + \phi_C^2 \beta_{AC} + \phi_B \phi_C(\beta_{AB} + \beta_{AC} - \beta_{BC})]$$

Equation 2.109

obtained by differentiating ΔG_{ABC} with respect to n_A. Careful examination of the above expression reveals that the two solute-solvent interaction parameters, β_{AB} and β_{AC}, can be calculated from the appropriate binary reduction

$$RT \ln (\phi_A^{sat})_B = RT\{\ln a_A^{solid} - 1 + (\phi_A^{sat})_B + V_A \Psi_B^{*}\} - V_A \phi_B^2 \beta_{AB}$$

Equation 2.110

and

$$RT \ln (\phi_A^{sat})_C = RT\{\ln a_A^{solid} - 1 + (\phi_A^{sat})_C + V_A\Psi_C^*\} - V_A\phi_C^2\beta_{AC}$$

Equation 2.111

and measured volume fraction solubilities in both pure alcohol cosolvents, $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$.

Zvaigzne et al[105] found that the Kretschmer–Wiebe model provides very accurate predictions for the solubility of anthracene dissolved in binary alcohol + alcohol solvent mixtures. Average absolute deviations between observed and predicted values were 1.4% for eq 2.109. For many of the systems they studied, the predictive error was less than the experimental uncertainty associated with the measured anthracene mole fraction solubilities. They then simplified the computations for the case of a sparingly soluble solute ($\phi_A^{sat} \approx 0$; $1 - \phi_A^{sat} \approx 1$) by completely eliminating the calculation of the two solute-solvent interaction parameters. Instead of calculating actual numerical values, eqs 2.110 and 2.111 are solved explicitly for β_{AB} and β_{AC}:

$$\beta_{AB} = RT\{ \ln[a_A^{solid}/(\phi_A^{sat})_B] - 1 + (\phi_A^{sat})_B + V_A\Psi_B^*\}/(V_A\phi_B^2)$$

Equation 2.112

and

$$\beta_{AC} = RT\{ \ln[a_A^{solid}/(\phi_A^{sat})_C] - 1 + (\phi_A^{sat})_C + V_A\Psi_C^*\}/(V_A\phi_C^2)$$

Equation 2.113

Equations 2.112 and 2.113 are substituted directly into eq 2.109. After suitable algebraic manipulation, the simplified expression

$$RT \ln \phi_A^{sat} = RT\{\phi_B^\circ[\ln(\phi_A^{sat})_B - V_A\Psi_B^*] + \phi_C^\circ[\ln(\phi_A^{sat})_C - V_A\Psi_C^*] +$$

$$V_A(\Psi_B + \Psi_C)\} + V_A\phi_B{}^{\circ}\phi_C{}^{\circ}\beta_{BC} \qquad \text{Equation 2.114}$$

is obtained. Both eqs 2.109 and 2.113 require $(\phi_A{}^{sat})_B$ and $(\phi_A{}^{sat})_C$ as input parameters. Thus, these equations can predict only solubility as a function of binary solvent composition. Zvaigzne et al compared the calculations for the simplified eq 2.113 with those from eq 2.109. They found there is essentially no difference regarding the predictive accuracy. Anthracene has a sufficiently low mole fraction (and volume fraction) solubility in alcohol cosolvents, and the infinite dilution approximation of $\phi_A{}^{sat} \approx 0$ is completely valid. This will not necessarily be the case in other studies that could involve more soluble polycyclic aromatic hydrocarbon solutes, such as pyrene and phenanthrene. It should be noted that the Kretschmer–Wiebe model cannot be extended easily to systems containing two alcohols or to systems which contain solute-solvent complexation, because the expressions for the concentration(s) of the alcohol monomers (ϕ_{B1} and/or ϕ_{C1}) cannot be solved in a closed mathematical form. Those calculations would require a very complicated re-iterative process.

Mecke–Kempter Association Model

Like the Kretschmer–Wiebe model, the Mecke–Kempter association model assumes the alcohol forms continuous hydrogen bonded polymers, $C_1, C_2, C_3, \ldots, C_i, \ldots$ by successive chemical reactions $C_i + C_1 \rightleftharpoons C_{i+1}$. It is described by a single isodesmic equilibrium constant of the form

$$K_C = \hat{\phi}_{C_{i+1}}/(\hat{\phi}_{C_i}\hat{\phi}_{C_1}) \qquad \text{Equation 2.115}$$

with the volume fraction of the *i*-mer calculated by using the molar volume of the monomer multiplied by *i*. An isodesmic equilibrium constant is defined as having identical numerical values for each consecutive, stepwise association. The Mecke–Kempter model differs from the Kretschmer–Wiebe model in that all concentrations in the equilibrium constant are expressed as volume fractions rather than as molarities.

The overall stoichiometric volume fraction of the alcohol (ϕ_C) is the sum of the volume fractions of each individual alcohol species

$$\phi_C = \Sigma\, \hat{\phi}_{C_i} = \Sigma\, \hat{\phi}_{C_1}(K_C \hat{\phi}_{C_1})^{i-1} = \hat{\phi}_{C_1}/(1 - K_C \hat{\phi}_{C_1}) \qquad \text{Equation 2.116}$$

For the series to converge, it is necessary that $|K_C \hat{\phi}_{C_1}| < 1$.

The chemical part of the Gibbs energy is based upon the Flory–Huggins athermal model, and may be written as

$$(\Delta G_{ABC}^{E})_{ch} = RT[\hat{n}_A \ln \hat{\phi}_A + \hat{n}_B \ln \hat{\phi}_B + \Sigma\, \hat{n}_{C_i} \ln \hat{\phi}_{C_i}]$$

Equation 2.117

The respective chemical potentials relative to the pure or hypothetical liquid components, μ_i°, are obtained through differentiation with respect to the number of moles of each chemical species

$$(\hat{\mu}_A - \mu^\circ_A)/RT = \ln \hat{\phi}_A + 1 - (V_A/\hat{V}_{soln}) \qquad \text{Equation 2.118}$$

$$(\hat{\mu}_B - \mu^\circ_B)/RT = \ln \hat{\phi}_B + 1 - (V_B/\hat{V}_{soln}) \qquad \text{Equation 2.119}$$

$$(\hat{\mu}_{C_i} - \mu^\circ_{C_i})/RT = \ln \hat{\phi}_{C_i} + 1 - (V_{C_i}/\hat{V}_{soln}) \qquad \text{Equation 2.120}$$

where $\hat{V}_{soln}$ is the true molar volume of the ternary solution

$$1/\hat{V}_{soln} = \hat{\phi}_A/V_A + \hat{\phi}_B/V_B + \Sigma\, \hat{\phi}_{C_i}/V_{C_i} = \phi_A/V_A + \phi_B/V_B + \ln(1 + K_C\phi_C)/K_C V_C$$

Equation 2.121

and for the pure alcohol

$$1/\hat{V}^*_{soln} = \ln(1 + K_C)/K_C V_C \qquad \text{Equation 2.122}$$

Several thermodynamic textbooks[3,14,106] demonstrate that the chemical potential of stoichiometric component C is equal to the chemical potential of the monomeric (uncomplexed) species in solution:

$$\hat{\mu}_{C_1} = \mu_C \qquad \text{Equation 2.123}$$

To obtain the customary mixing properties, pure substance C must be taken as the new reference state:

$$(\mu_C - \mu^*_C)/RT = \ln(\hat{\phi}_{C_1}/\hat{\phi}^*_{C_1}) - (V_C/\hat{V}_{soln}) + (V_C/\hat{V}^*_{soln})$$

Equation 2.124

By combining eqs 2.119–2.122, the following expression for $(\Delta G_{ABC})_{ch}$ is obtained:

$$(\Delta G_{ABC})_{ch} = RT\{n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln(\hat{\phi}_{C_1}/\hat{\phi}^*_{C_1}) -$$

$$[(n_A V_A + n_B V_B + n_C V_C) \ln(1 + K_C\phi_C)/K_C V_C] + n_C \ln(1 + K_C)/K_C\}$$

Equation 2.125

The simplest equation that might be expected adequately to describe the physical contributions to the excess Gibbs energy $(\Delta G^E_{ABC})_{ph}$ is

$$(\Delta G^E_{ABC})_{ph} = (\hat{n}_A V_A + \hat{n}_B V_B + \Sigma\, \hat{n}_{C_i} V_{C_i})^{-1} x$$

$$[\hat{n}_A V_A\, \hat{n}_B V_B A_{AB} + \Sigma\, \hat{n}_A V_A\, \hat{n}_{C_i} V_{C_i} A_{AC_i} + \Sigma\, \hat{n}_B V_B\, \hat{n}_{C_i} V_{C_i} A_{BC_i}]$$

Equation 2.126

where the A_{ij} terms represent binary interaction parameters. Because eq 2.86 contains far too many parameters for useful applications, reasonable assumptions must be used to reduce greatly the number of parameters. Treatment of the A_{AC_i} and A_{BC_i} interaction parameters in a manner similar to that employed by Bertrand[107] for the chloroform-triethylamine complex leads to

$$A_{KC_i} = (\delta_K' - \delta_{C_i}')^2 \text{ where K = A, B} \qquad \text{Equation 2.127}$$

$$\delta_{C_{i+1}}' = (V_{C_i}\delta_{C_i}' + V_{C_i}\delta_{C_1}')/(V_{C_i} + V_{C_1}) = (i\delta_{C_i}' + \delta_{C_1}')/(i + 1) = \delta_{C_1}'$$

Equation 2.128

$$A_{KC_i} = A_{KC_1} \text{ where K = A, B} \qquad \text{Equation 2.129}$$

where δ_i' is the modified solubility parameter of component *i*. The combination of eqs 2.124–2.127 enables $(\Delta G_{ABC}^{E})_{ph}$ to be expressed as

$$(\Delta G_{ABC}^{E})_{ph} = (n_A V_A + n_B V_B + n_C V_C)^{-1} \times$$

$$[n_A V_A n_B V_B A_{AB} + n_A V_A n_C V_C A_{AC_1} + n_B V_B n_C V_C A_{BC_1}]$$

Equation 2.130

in terms of three binary interactional parameters. We obtain the following expression for the total Gibbs energy of the ternary system (per stoichiometric mole of solution) by substituting eqs 2.126 and 2.130 into eq 2.72:

$$\Delta G_{ABC} = RT\{\chi_A \ln \phi_A + \chi_B \ln \phi_B + \chi_C \ln(\phi_{C_1}/\hat{\phi}^{*}_{C_1}) -$$

$$[(\chi_A V_A + \chi_B V_B + \chi_C V_C) \ln(1 + K_C\phi_C)/K_C V_C] + \chi_C \ln(1 + K_C)/K_C\} +$$

$$(\chi_A V_A + \chi_B V_B + \chi_C V_C) \times [\phi_A \phi_B A_{AB} + \phi_A \phi_C A_{AC_1} + \phi_B \phi_C A_{BC_1}]$$

Equation 2.131

Thermodynamic principles relate solubility to chemical potential. For a system obeying eq 2.17, the solubility of a sparingly soluble solute ($\phi_A^{sat} \approx 0$) is

$$RT \ln a_A^{solid} = RT[\ln \phi_A^{sat} + \phi_B^{\circ}(1 - V_A/V_B) + \phi_C^{\circ}(1 - V_A \ln(1 + K_C\phi_C^{\circ})/K_C V_C \phi_C^{\circ})] +$$

$$V_A[\phi_B^{\circ} A_{AB} + \phi_C^{\circ} A_{AC_1} - \phi_B^{\circ}\phi_C^{\circ} A_{BC_1}] \qquad \text{Equation 2.132}$$

obtained by differentiating ΔG_{ABC} with respect to n_A. Careful examination of the above expression reveals that the A_{AB} and A_{AC_1} parameters can be eliminated from the basic model via

$$RT \ln a_A^{solid} = RT[\ln(\phi_A^{sat})_B + (1 - V_A/V_B)] + V_A A_{AB}$$

Equation 2.133

and

$$RT \ln a_A^{solid} = RT[\ln(\phi_A^{sat})_C + 1 - V_A \ln(1 + K_C)/K_C V_C] + V_A A_{AC_1}$$

Equation 2.134

where $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$ denote the volume fraction solubilities in the two pure solvents. By substituting these terms, one obtains a relatively simple mathematical expression for the solubility in binary hydrocarbon + alcohol solvent mixtures

$$\ln \phi_A^{sat} = \phi_B^{\circ} \ln(\phi_A^{sat})_B + \phi_C^{\circ} \ln(\phi_A^{sat})_C + (V_A/K_C V_C) \times [\ln(1 + K_C\phi_C^{\circ}) -$$

$$\phi_C^{\circ} \ln(1 + K_C)] + V_A \phi_B^{\circ} \phi_C^{\circ} (\delta_B' - \delta_C')^2 (RT)^{-1} \qquad \text{Equation 2.135}$$

that does not require a prior knowledge of the enthalpy of fusion and melting point of the solute. For the purposes of computation, the solvent-solvent pairwise interactional

parameter has been approximated by using modified solubility parameters to reduce the number of unknown "adjustable" parameters from the predictive expression. In addition, the derived expression correctly describes the solubility in the pure complexing and non-complexing solvents. It also can be used to calculate the "optimum value" of the solvent-solvent self-association constant from the measured solubility as a function of solvent composition.

Despite the complex appearance of eq 2.135, its application to solubilities in mixed solvents is relatively straightforward. The quantities $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$ are calculated from the measured mole fraction solubility of the solid in the pure solvents, assuming that the excess molar volume (or the volume change upon mixing) is zero. These quantities, along with the molar volumes, modified solubility parameters, and an assumed value for the equilibrium constant, are used then in eq 2.135 to calculate ϕ_A^{sat} at each binary solvent composition. Once again, the calculations can be repeated until the numerical value of K_C that best describes the experimental solubility in a particular binary solvent system is obtained.

Two points about K_C computations and solubility predictions should be noted before illustrating the application of eq 2.135. First, in systems having very weak solvent self-association ($K_C \approx 0$), both logarithmic terms can be expanded as

$$\ln(1 + x) = x - (1/2)x^2 + (1/3)x^3 - (1/4)x^4 + \ldots \qquad \text{Equation 2.136}$$

with only the first term in each series being retained. Higher-order terms become vanishingly small for values of x near zero, at which contributions from the two logarithmic terms cancel

$$(V_A/K_CV_C)[\ \ln(1 + K_C\phi_C^\circ) - \phi_C^\circ \ln(1 + K_C)] = (V_A/K_CV_C)[K_C\phi_C^\circ - K_C\phi_C^\circ] = 0$$

Equation 2.137

and eq 2.135 is mathematically equivalent to the infinite dilution form of eq 2.54 of the Extended NIBS model with $K_{AC} = 0$, whenever

$$G_{BC}^{fh} = (\chi_B^\circ V_B + \chi_C^\circ V_C)\phi_B^\circ\phi_C^\circ(\delta_B' - \delta_C')^2$$

(G_{BC}^{fh} is the excess molar Gibbs energy relative to the Flory-Huggins model.)

Second, it can be shown that the other limiting case, namely $K_C \rightarrow \infty$,

$$\lim_{Kc\rightarrow\infty}\{[V_A \ln(1 + K_C\phi_C^\circ)/K_CV_C] - [V_A\phi_C^\circ \ln(1 + K_C)/K_CV_C)]\}$$

Equation 2.138

also reduces to eq 2.25 with $K_{AC} = 0$. Since both terms of the above bracketed expression yield the indeterminant form of ∞/∞, one applies l'Hospital's rule to give

$$\lim_{Kc\rightarrow\infty}[V_A\phi_C^\circ/V_C(1 + K_C\phi_C^\circ) - V_A\phi_C^\circ/V_C(1 + K_C)] = 0 \qquad \text{Equation 2.139}$$

From a thermodynamic standpoint, these observations indicate that component C behaves as a single chemical entity both in the absence of self-association and in instances of extremely strong self-association. For intermediate K_C values, the number of monomers, dimers, etc., depends upon binary solvent composition. The net contribution from the two logarithmic terms is positive. Therefore, there may be several K_C values that give comparable descriptions for the observed solubility data in any given binary solvent system. This depends upon the shape of the % deviation versus K_C two-dimensional surface.

Acree et al.[108] compared measured anthracene solubility in 30 binary alkane + alcohol solvent mixtures taken from the chemical literature[81] to predicted values based on eq 2.135. The modified solubility parameters they used accounted only for nonspecific interactions, thus removing the case of hydrogen-bonding contributions for the alcohols. The same exists in the case of the Kretschmer–Wiebe model. Numerical values of $\delta_{solvent}'$ were obtained from published compilations.[82,84] They were deduced by regressing solubility data of solid *n*-alkanes in organic solvents in accordance with the configurational entropic model of Huyskens and Haulait–Pirson.[109] This model differs slightly in mathematical form from the Flory–Huggins model from which eq 2.135 is derived. Different numerical values of K_C for each of the six cosolvents studied gave a non-unique description for the behavior of anthracene in the pure alcohols. This violated the basic assumption used in deriving eq 2.135. Therefore, they found that the Mecke–Kempter model provides reasonably accurate predictions of the solubility behavior of anthracene in these rather nonideal solvents. Generally speaking, deviations are on the order of approximately 15% or less. They also examined the numerical value of K_C that "best" described each system, along with the corresponding average absolute deviations. They felt that the additional complexity in calculating anthracene solubilities that were introduced with additional "curve-fit" parameters for small improvements in predictive ability was not warranted. They were unable to state definitely why K_C varies, but they did note that molecular interactions in these systems are undoubtedly more complex than those incorporated into their particular version of the Mecke–Kempter

theory. The aromatic hydrocarbon solute, anthracene, is assumed to be inert and is not permitted to form association complexes with either the monomeric alcohol or any of the presumed polymeric entities. Mecke-Kempter theory is viewed as providing a reasonable thermodynamic description of anthracene dissolved in binary alkane + alcohol mixtures with predictions to within an overall average deviation of approximately 9.4%. Also, it should also be noted that the Mecke-Kempter model cannot be extended easily to systems containing two alcohols or to systems which contain solute-solvent complexation, because the expressions for the concentration(s) of the alcohol monomers (ϕ_{B1} and/or ϕ_{C1}) cannot be solved in a closed mathematical form. Those calculations would require a very complicated re-iterative process.

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CHAPTER III

EXPERIMENTAL METHOD

In this study, the solubility of anthracene was measured in ternary solvent systems that consist of an alkane, an ether, and an alcohol. Previous studies[1-4] have shown that through hydrogen bonding, alcohols form long chains. When an alcohol bonds with the oxygen in the ether linkage, the chain is broken because there is no hydroxylic hydrogen. The three ethers chosen were dibutyl ether, methyl t-butyl ether, and 1.4-dioxane. Dibutyl ether was chosen because it is a symmetrical molecule with a relatively short chain on either side of the ether linkage. Methyl t-butyl ether is an asymmetrical molecule with a bulky group on one side of the ether linkage and a small methyl group on the other side. 1,4-Dioxane is a six-membered ring structure with two ether linkages and stable chair and boat configurations. Because no study has been done previously with ether groups, we chose one that was symmetrical, one that was asymmetrical with a bulky group on one side, and one that had twice the number of ether linakges.

The three alkanes studied were cyclohexane, heptane, and 2,2,4-trimethylpentane. Cyclohexane was chosen because of the symmetrical ring structure. Heptane is a straight-chain hydrocarbon. 2,2,4-Trimethylpentane is a branched hydrocarbon with a bulky group on one end. In that saturated hydrocarbons do not participate in hydrogen bonding, it was not expected that anthracene would be very soluble in solutions

consisting predominantly of these three alkanes. These particular three hydrocarbons were chosen because they are all relatively simple hydrocarbons with different structures.

The five alcohols chosen were 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol. Two additional systems with 2-pentanol were also measured, but there was not time to study all the possibilities of this alcohol with the chosen alkanes and ethers. 1-Propanol and 1-butanol are both homologs of a straight chain with the functional hydroxyl group on the first carbon atom. 2-Propanol, 2-butanol, and 2-pentanol are homologs of a straight chain molecule with the functional hydroxyl group on the second carbon atom. The final alcohol chosen, 2-methyl-1-propanol, is a short bulky molecule. These alcohols were selected to compare the effect of the length of chain, the position of the functional group on the chain, and the effect of a bulky group near the functional group. Each of the forty-five possible combinations (excluding 2-pentanol) consisted of one alcohol, one alkane, and one ether was studied.

The anthracene was obtained from two sources. Anthracene, obtained from Acros (99.9+%), was recrystallized three times from 2-propanone. The anthracene (Aldrich, 99.9+%) was used as received. 1-Propanol (Aldrich, HPLC, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99.5+%, anhydrous), heptane (Aldrich, HPLC, 99+%), cyclohexane (Aldrich, HPLC, 99.9+%), 2.2.4-trimethylpentane (Aldrich, HPLC, 99.7+%), dibutyl ether (Aldrich, 99.3+%, anhydrous), methyl t-butyl ether (Arco, 99.9%), and 1,4-dioxane (Aldrich, 99.8%, anhydrous), were

stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better.

Before beginning to analyze the solutions of unknown concentrations of anthracene, a series of standard solutions was prepared. Approximately 0.1 g (mass known to the nearest 0.0001 g) of anthracene was dissolved in acetone in a 50 mL volumetric flask. This standard solution was made approximately once a week and became the stock standard for the week. A 5.0 ml aliquot of this stock standard was volumetrically diluted to 100 ml in a second volumetric flask with methanol or isopropanol. From this diluted solution, eight standard solutions were prepared by further diluting 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 ml with methanol or isopropanol in eight different 25.0 ml volumetric flasks. Equation 3.1 was used

$$[(m/178.23)/0.050](5/100(V/25)=C_{anthracene} \qquad \text{Equation 3.1}$$

to determine the concentration, $C_{anthracene}$, in each standard solution. The factor inside the brackets in eq 3.1 gave us the concentration of the standard stock solution with the m replacing the mass of anthracene (in grams) dissolved in the standard solution. The molecular mass of anthracene is 178.23 g mol^{-1}. The size volumetric flask used was 50 mL or so. The second factor is the dilution in the 100 mL flask, with both numbers being measured in mL. The final dilution factor is the measured volume, V, of the solution removed from the 100 mL flask and diluted to 25 mL. The anthracene concentrations ranged from C/mol L^{-1} = 6.75 X 10^{-5} to C/mol L^{-1} = 2.25 X 10^{-4}. New standards were prepared each day for analyses on the solutions of unknown concentrations. The

combined Beer-Lambert law,[5] eq 3.2, was used to calculate the molar absorptivity for each standard solution.

$$A = \varepsilon bc \qquad \text{Equation 3.2}$$

In eq 3.2, A is the measured absorbance, ε is the molar absorptivity in units of $cm^{-1}mol^{-1}L$, b is the path length of light passing through the solution, and c is the concentration of the solution given in mol L^{-1}. The quartz cuvettes used in the analysis were 1.0 cm^2, hence b = 1.0 cm. The measured absorbances for these standard solutions varied systematically with molar concentration. From this, the molar absorptivities were calculated and ranged from $\varepsilon/(L\ mol^{-1}cm^{-1}) = 7450$ to $\varepsilon/(L\ mol^{-1}\ cm^{-1}) = 7150$. In theory, the molar absorptivity should remain constant as the concentration varies. In practice, there are minor deviations in linearity in the molar absorptivity with this varying concentration. As a result, the value of ε is chosen to correspond to the absorbance of the unknown solution.

There are three types of deviations from the Beer-Lambert law (also known as Beer's law). First, there are the real deviations that are just fundamental and represent limitations. Beer's law is successful in describing the absorbance only in dilute solutions (usually < 0.01 M).[6] For higher concentrations, the distance between the molecules of the absorbing species becomes small enough to affect the charge distribution of their neighbors. This interaction can affect the species ability to absorb a given wavelength of radiation.

Second, there are the apparent chemical deviations from Beer's law. When an analyte associates, dissociates, or reacts with a solvent to produce a product having a

different absorption spectrum from the analyte, deviations from Beer's law appear. This happens frequently with acid/base indicators. The color change that occurs with a change in acidity indicates a shift in the equilibrium away from the analyte that is being measured.[7]

Third, apparent instrumental deviations occur primarily from the use of polychromatic radiation. Beer's law is observed only with truly monochromatic radiation. Unfortunately, this is seldom practical. Devices that use a continuous source try to isolate a band of output. This produces a more or less symmetric band of wavelengths around the desired one. Experimentally, it has been shown that deviations from Beer's law resulting from the use of a polychromatic bean are not significant in most cases. Another source of deviation from Beer's law is stray radiation, a contaminant in the radiation exiting from a monochromator. Stray radiation often has a wavelength that differs greatly from the radiation exiting the slit and passing through the sample. However, there is no way to know if the stray radiation actually passed through the sample. These deviations from Beer's law from instrumental sources always lead to negative absorbance errors.[8]

For each system studied, nineteen solutions were prepared volumetrically, as indicated in Table I. These solutions were composed to evaluate adequately the range of mole fractions from 0.1 to 0.9 for each component. The ternary solvent mixtures were weighed after the addition of each solvent, so compositions could be calculated to 0.0001 mole fraction. The solvent mixture and excess solute (totaling approximately 20 mL) were placed in 25 mL amber glass bottles and sealed with parafilm. Electrical tape was

used to hold the parafilm in place. Then, rubber bands were placed around the tape to keep the tape in place. The bottles were then heated in a water bath at approximately 40°C for a minimum of 4½–5 hours, depending on the beginning temperature of the water bath. After the heating period, the bottles were transferred to a constant temperature water bath at (25.0±0.1)°C and allowed to equilibrate with periodic agitation for at least three days (often longer). Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days. No corrections were necessary for the 5 mL headspace in the amber bottles. The solvent that partitioned between the liquid and vapor phases was neglected because it would affect only the fourth decimal place of the calculated mole fraction.

A minimum of four aliquots of saturated anthracene solutions (in the range of 0.25–0.60 mL) was transferred by syringe into separate, tared 50 ml volumetric flasks. See James for a more complete discussion of the difficulties and remedies for preparing solutions for analysis, mechanisms of equilibrating solutions, and withdrawing an aliquot from a saturated solution in equilibrium.[9] Each flask was weighed before and after the addition of the aliquot to determine the mass of sample for analysis. The samples were then diluted quantitatively with methanol or isopropanol for spectrophotometric analysis at 356 nm on a Bausch and Lomb Spectronic 2000. The absorbance was recorded for each solution.

Instrumentation

Molecular ultraviolet/visible absorption spectroscopy is used primarily for quantitative analysis. It is probably used more widely in chemical and clinical

laboratories throughout the world than any other single procedure. Important characteristics of spectrophotometric methods are

(a) Wide applicability. Approximately 90% of analyses performed in clinical laboratories are based on ultraviolet and visible absorption spectroscopy because of the huge numbers of inorganic, organic, and biochemical species that absorb in the ultraviolet and visible regions of the electromagnetic spectrum. Many nonabsorbing species can be converted to absorbing species through chemical conversion.

(b) High sensitivity. Typical detection limits for absorption spectroscopy range from 10^{-4} to 10^{-5} M.

(c) Moderate to high selectivity. Frequently, a wavelength can be found from which only the desired chromophore absorbs, thus eliminating the need to perform separations to isolate the desired chromophore.

(d) Good accuracy. The relative errors in determined concentrations often lie in the range of 1–5%. These errors often can be reduced with special procedures.

(e) Ease and convenience. Spectrophotometric measurements are easily and rapidly performed, and lend themselves to automation.[10]

Even when two UV active chromophores that do not interact are in the same solution, we know that the total UV absorption is the sum of the absorptions of the two individual chromophores.[11] Additional testing would be necessary to determine the amount of only one of the two chromophores.

The Bausch and Lomb Spectronic 2000 used for our data collection is an example of a double-bean recording spectrophotometer for the ultraviolet and visible regions. Basically, there is a reference cell and a sample cell. In our case, the reference cell contained either methanol or isopropanol, determined by whichever solvent was used to dilute the solution. The light from the source was passed through an aperture, through a filter to select the desired wavelength, and then to an optical chopper to split the single beam into two beams. Each of the beams passed through one cell. After passing through the cuvette, the light was recombined by subtracting the signal exiting the reference cell from the signal exiting the sample cell. From there, the signal was sent to the detector where a read out of the absorbance was displayed.

The Bausch and Lomb Spectronic 2000 used in our research proved to be a rugged and durable instrument, presenting few problems over the course of this research. This instrument compensated for most all fluctuations in the radiant output of the source, as well as for drift in the detector and the amplifier. It also compensated for wide variations in source intensity with wavelength. The double-beam design lended itself well to the continuous recording transmittance or absorbance spectra. A thorough discussion of the weekly routine of preventative maintenance and practical solutions for occurring problems is given by Edisbury.[12]

Light is absorbed by two types of electrons:

(1) shared electrons that directly participate in bond formation, and thus, are associated with more than one atom, and

(2) unshared electrons that are localized largely about electronegative atoms, such as oxygen, the halogens, sulfur, and nitrogen.

Shared electrons, such as those found in the double bonds of anthracene, are bound so loosely, that their excitation energies correspond to wavelengths in the readily accessible ultraviolet region. The unsaturated organic functional groups that absorb in the ultraviolet and visible regions are termed chromophores. In our case, anthracene is our chromophore with maximum absorption at a wavelength of 356 nm.[13,14] All other components in the solutions contained only single bonds. The electrons in single bonds are held so firmly that their excitation energies require absorption wavelengths in the vacuum ultraviolet region (below 180 nm). Thus, no other chromophore interfered with our measurement of the anthracene in solution.

Calculations

After each sample was analyzed, and the absorbance for that sample was recorded in the lab notebook, a value of the molar absorptivity, ε, was chosen from a working curve of molar absorptivities versus solution concentration, as determined from the standard solutions for that set of analyses. By remembering that the path length, b, through which the radiation passes, is equal to 1.0 cm, and by rearranging eq 3.2, we were able to calculate the concentration of anthracene in the unknown saturated solution by dividing the absorbance by the molar absorptivity.

$$C_{anthracene} = A/\varepsilon \qquad \text{Equation 3.3}$$

From this, we calculated the weight percent of anthracene in the unknown saturated solution.

$$\text{wt \%}_{\text{anthracene}} = (\text{wt of anthracene/total weight of sample analyzed})*100\%*\text{DF}$$

Equation 3.4

$$\text{wt \%}_{\text{anthracene}} = (178.23)(0.050)(C_{\text{anthracene}})(100\%)/\text{weight of sample}$$

Equation 3.5

In this equation, 178.23 g mol^{-1} is the formula weight for anthracene, the factor 0.050 is the volume of the volumetric flask in liters to which the sample was originally transferred to, wt of sample is the amount of sample analyzed, and DF is the dilution factor. With this information, we were prepared to calculate the mole fraction compositions of the ternary solvent mixtures.

$$\chi^{\bullet}_{\text{ether}} = (wt_{\text{ether}}/MW_{\text{ether}})/[(wt_{\text{ether}}/MW_{\text{ether}}) + (wt_{\text{alkane}}/MW_{\text{alkane}}) + (wt_{\text{alcohol}}/MW_{\text{alcohol}})]$$

Equation 3.6

$$\chi^{\bullet}_{\text{alkane}} = (wt_{\text{alkane}}/MW_{\text{alkane}})/[(wt_{\text{ether}}/MW_{\text{ether}}) + (wt_{\text{alkane}}/MW_{\text{alkane}}) + (wt_{\text{alcohol}}/MW_{\text{alcohol}})]$$

Equation 3.7

$$\chi^{\bullet}_{\text{alcohol}} = (wt_{\text{alcohol}}/MW_{\text{alcohol}})/[(wt_{\text{ether}}/MW_{\text{ether}}) + (wt_{\text{alkane}}/MW_{\text{alkane}}) + (wt_{\text{alcohol}}/MW_{\text{alcohol}})]$$

Equation 3.8

In these equations, $\chi_i^{\bullet}$ is the mole fraction of one of the solvents, i, in the ternary mixture, wt_i represents the weight of that solvent, i, in the original preparation of the solution, and MW_i represents the molecular weight for that $solvent_i$. These three mole fractions should add up to 1.0 since they represent the entire solvent mixture before any solute is added.

Knowing the mole fraction composition, we computed an average "molecular weight" for the ternary solvent mixture.

$$MW_{solvent\ mix} = \chi^{\bullet}_{ether} MW_{ether} + \chi^{\bullet}_{alkane} MW_{alkane} + \chi^{\bullet}_{alcohol} MW_{alcohol}$$

Equation 3.9

We were then in position to calculate the mole fraction of anthracene.

$$\chi_{anthracene} = (wt\ \%_{anthracene}/MW_{anthracene})/[(wt\ \%_{anthracene}/MW_{anthracene}) + (100 - wt\ \%_{anthracene})/MW_{solvent\ mix})]$$

Equation 3.10

In this equation, for the $wt\ \%_{anthracene}$ we substituted the number calculated in eq 3.4. For $MW_{solvent\ mix}$ we substituted the number calculated using eq 3.8. This provides the calculation for the mole fraction for each substance in the solution. The mole fraction composition for each system studied can be found in Tables II through XLVIII.

TABLE I

Volume (mL) of Each Solvent Component in Ternary Solvent Mixtures

Solution Number	Solvent Ether (mL)	Solvent Alcohol (mL)	Solvent Alkane (mL)
1.	7	7	7
2.	3	3	14
3.	3	14	3
4.	14	3	3
5.	5	5	10
6.	10	5	5
7.	5	10	5
8.	2	4	14
9.	14	2	4
10.	2	14	4
11.	14	4	2
12.	4	2	14
13.	4	14	2
14.	2	8	10
15.	2	10	8
16.	8	2	10
17.	8	10	2
18.	10	2	8
19.	10	8	2

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CHAPTER IV

INTERPRETATION OF DATA

The NIBS/Redlich–Kister Equation for Ether + Alcohol + Alkane Ternary Solvent Mixtures

Acree and co-workers[1-3] suggested the combined NIBS/Redlich–Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems. For a ternary solvent system, the mathematical representation takes the form of eq 2.70. Each summation starts at zero. If three coefficients are needed to describe adequately the solubility of anthracene in the BC sub-binary solvent system, then the summation would go to 2. Recent studies have shown that eq 2.70 provides reasonably accurate predictions for anthracene solubilities in ternary two alkane + alcohol[4,5] and alkane + two alcohol[6-8] solvent mixtures. Such systems exhibit fairly large deviations from solution ideality arising from the self-association of each alcohol cosolvent. In mixtures containing two alcohol cosolvents, the deviations are also from the formation of heterogeneous hydrogen-bonded chains between the dissimilar alcohol molecules which were studied.

As part of the dissertation research, anthracene solubilities were measured in forty-five ternary solvent mixtures containing an alcohol, ether, and alkane cosolvent. Unlike the ternary two alkane + alcohol and alkane + two alcohol solvent mixtures

studied previously, hydrogen bond formation is terminated each time that an alcohol molecule hydrogen bonds with the ether cosolvent. The measured anthracene mole fraction solubilities can be used to test the limitations and applications of thermodynamic association models as there is virtually no solubility data in the published literature in ternary associating solvent mixtures except for the data of Deng et al.[4-11]

In reporting experimental solubility data, it is very important to make certain that the values were determined accurately. Analysis of replicate samples showed that the measured values were reproducible to ± 1.5%. Experimental measurements were made after the solutions had equilibrated at least three days in a constant temperature bath. Select samples were re-analyzed two to three days later to ensure that equilibrium had been reached. In all cases, the subsequent measurements were within ± 1.5% of the original values.

The replicate analyses, and subsequent analyses on select samples, that were performed are not capable of determining whether or not there were any mistakes made in preparing the original ternary mixtures. For example, let's suppose that in weighing the amount of solvent C there was a transposed digit. The weight of the amber glass bottle plus solvent C was mistakenly recorded as 43.5261 grams, rather than 45.3261 grams. No matter how many times one measured the dissolved anthracene concentration inside the bottle, one would not detect that the solvent composition was in error. To detect such errors, one needs to employ internal consistency tests.

Thermodynamicists often employ thermodynamic consistency tests to ensure the measured data's internal consistency. Isothermal binary-liquid equilibria are tested using

the integral form of the Gibbs–Duhem equation. Binary excess enthalpy data is tested by showing that the measured values can be described mathematically by the Redlich–Kister equation. The Redlich–Kister equation obeys the Gibbs–Duhem equation. Thermodynamic consistency tests for ternary, quaternary, and higher-order multicomponent mixtures are more difficult to use. What is generally done in the case of ternary, quaternary, etc. mixtures is to show that experimental values can be predicted with reasonable accuracy using solution models that are known to obey the Gibbs–Duhem equation.

The Redlich–Kister equation was developed by Acree and co-workers for the mathematical representation of isothermal solubility data for solutes dissolved in binary solvent mixtures. As noted by the authors, outlier data points in need of remeasurement would be identified because they would deviate significantly from the mathematical equation generated by regressing the measured solubility data in accordance with the Combined NIBS/Redlich–Kister equation. The ternary solvent form of the Combined NIBS/Redlich–Kister equations is going to be used to assess the internal consistency of the measured anthracene solubility data for alcohol + ether + alkane mixtures. The equation will be used to predict the solubility behavior of anthracene in all 45 ternary systems studied. Any experimental data point that differs significantly from the predicted value will be considered suspect.

The solubility of anthracene in the ternary methyl *tert*-butyl ether (B) + 2-propanol (C) + heptane (D) at $\chi_B^\circ = 0.2981$ and $\chi_C^\circ = 0.4593$ will be predicted to illustrate the computational method. Published papers have reported the calculated S_i

parameters for anthracene dissolved in sub-binary systems[8,12-18] ($S_{0,B\text{-}C}$ = 1.976, $S_{1,B\text{-}C}$ = –0.514, and $S_{2,B\text{-}C}$ = 0.651 for the methyl *tert*-butyl + 2-propanol sub-binary system; $S_{0,B\text{-}D}$ = 0.149 and $S_{1,B\text{-}D}$ = 0.268 for the methyl *tert*-butyl ether + heptane sub-binary system; and $S_{0,C\text{-}D}$ = 1.491, $S_{1,C\text{-}D}$ = 0.587, and $S_{2,C\text{-}D}$ = 0.566 for the 2-propanol + heptane sub-binary system), as well as the measured mole fraction solubilities (χ_A^{sat} = 0.003050 for methyl *tert*-butyl ether, χ_A^{sat} = 0.000411 for 2-propanol, and χ_A^{sat} = 0.001571 for heptane). The specific form of the NIBS/Redlich–Kister prediction for the solubility of anthracene (A) in a ternary solvent system consisting of methyl *tert*-butyl ether (B) + 2-propanol (C) + heptane (D) is

$$\ln \chi_A^{sat} = \chi_B \ln(\chi_A^{sat})_B + \chi_C \ln(\chi_A^{sat})_C + \chi_D \ln(\chi_A^{sat})_D +$$
$$\chi_B \chi_C [S_{0,B\text{-}C} + S_{1,B\text{-}C}(\chi_B - \chi_C) + S_{2,B\text{-}C}(\chi_B - \chi_C)^2] +$$
$$\chi_B \chi_D [S_{0,B\text{-}D} + S_{1,B\text{-}D}(\chi_B - \chi_D)] +$$
$$\chi_C \chi_D [S_{0,C,D} + S_{1,C\text{-}D}(\chi_C - \chi_D) + S_{2,C\text{-}D}(\chi_C - \chi_D)^2] \qquad \text{Equation 4.1}$$

The various binary coefficients and solvent mole fraction compositions are substituted into eq 4.1 to find the predicted value for the anthracene solubility.

$$\ln \chi_A^{sat} = 0.2981 \ln(.003050) + 0.4593 \ln(0.000411) + 0.2426 \ln(0.001571) +$$
$$(0.2981)(.4593)[1.976 + (–0.514)(0.2981 – 0.4593) + 0.651(0.2891 – 0.4593)^2] +$$
$$(0.2981)(0.2426)[0.149 + 0.268(0.2981 – 0.2426)] +$$
$$(0.4593)(0.2426)[1.491 + 0.587(0.4593 – 0.2426) + 0.566(0.4593 – 0.2426)^2] = – 6.3945$$

Thus, the predicted value for χ_A^{sat} = 0.001671. From Table XXXXIII the measured value is 0.001647. This gives a deviation of

$$\text{deviation} = 100 \times [(\chi_A^{sat})_{predicted} - (\chi_A^{sat})_{measured}]/(\chi_A^{sat})_{measured}$$

$$= 100 \times (0.001671 - 0.001647)/0.001647 = 1.46\%$$

Equation 4.2

These calculations were made for each of the nineteen data points for the methyl *tert*-butyl + 2-propanol + heptane system. An overall average of 1.85% was obtained.[12] This is comparable to the experimental uncertainty of 1.5%. For the 45 systems studied[12,19-26], eq 2.70 provides very accurate predictions of the observed solubility behavior of anthracene in a ternary solvent system consisting of an ether, an alcohol, and an alkane. The computations did not find any experimental values in need of remeasurement.

Mobile Order Theory

Basic Assumptions of the Model

Historically, Einstein was the first to propose the calculation of thermodynamic probability using time fractions.[27-29] Not much attention was paid to his proposal until Huyskens[29-41] and Ruelle[42-56] proposed Mobile Order theory as an alternative thermodynamic description of molecular complexation.

This basic model[28-58] expresses the equilibrium condition in terms of the time fractions for the period of time a given molecule in a grouping is “free” or “bonded”, as opposed to the concentrations of the various associated species believed to be present. The model assumes all molecular groups perpetually move in the liquid, and that

neighbors of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume V of the liquid divided by the number N_A molecules of the same kind, i.e., Dom A = V/N_A. The center of this domain perpetually moves. The highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential contacts lead to deviations with respect to this "random" visiting. This is especially true in the case of hydrogen bonding. It requires a hydroxylic hydrogen atom follows the proton acceptor of a neighboring molecule in its walk through the liquid most of the time. What originates is a kind of "mobile order."

Mobile Order For Systems Involving A Solute Dissolved In A Neat Solvent

The quantitative development of the assumptions which form the basis of Mobile Order Theory led to the derivation of a universal equation by Ruelle et al.[54] for the solubility. This equation for solubility, given in terms of volume fraction ϕ_A^{sat} of the solute, interprets the different enthalpic and entropic contributions to the Gibbs energy change when a solute A is dissolved in a solvent S. In addition, the authors derived expressions describing the influence of solvent-solvent, solute-solvent, and solute-solute interactions for the chemical potential of the solute. The equation successfully predicts the solubility of naphthalene[47] in both polar and nonpolar solvents. In the case of nonpolar solvents, hydrogen bonding between solute and solvent was ignored, and the

solubility of naphthalene in volume fraction ϕ_A^{sat} was expressed by the product of three terms

$$\phi_A = e^{-A}e^{B}e^{-D} \qquad \text{Equation 4.3}$$

Equation 4.3 accounts for the ideal solubility, the entropy of mixing, the changes arising in the nonspecific cohesion forces upon mixing, and the hydrophobic effects of the associated solvents such as alcohols on the solubility of an inert substance. Each term in eq 4.3 has a well-defined expression to represent a physical phenomenon.

The fluidization constant A represents the breaking of solute-solute interactions in the crystalline lattice that must occur for the solute to dissolve. The fluidization constant is not always a simple mathematical expression. If there are no solid-solid transitions between the melting point temperature, T_{mp}, and the solution temperature, then the fluidization constant can be calculated from

$$A = -\ln a_A^{solid} = \Delta H_A^{fus}(1/T - 1/T_{mp})/R + \Delta C_p[(T_{mp}/T - 1) - \ln(T_{mp}/T)]/R$$

Equation 4.4

where ΔH_A^{fus} is the molar enthalpy of fusion for the solute at its normal melting point temperature, T_{mp}, and ΔC_p is the difference in the heat capacity between the crystalline and the molten forms of the substance. Equation 4.4 assumes that the difference in heat capacities between the solid and the supercooled liquid solute remains constant over the temperature range from T to T_{mp}. If the solutes are not removed too far from their normal melting point temperature, the term $(T_{mp}/T - 1)$ is approximately equal to $\ln T_{mp}/T$. Because ΔC_p is usually unknown, a first approximation of the fluidization constant is

$$A = -\ln a_A^{solid} = \Delta H_A^{fus}(1/T - 1/T_{mp})/R \qquad \text{Equation 4.5}$$

without any significant loss of accuracy. Inspection of eq 4.5 shows the ideal solubility of a crystalline solute decreases as both the molar enthalpy of melting of the crystal increases and as the difference between the melting point and the actual temperature, T, increases.

The B term in eq 4.3 is a correction term that is obtained by differentiating the configuration entropy contribution to the Gibbs energy with respect to the number of moles of solute. In Mobile Order theory, the entropy of mixing is assumed to be

$$\Delta S^{mix} = 0.5RT[\chi_A \ln \chi_A + \chi_S \ln \chi_S + \chi_A \ln \phi_A + \chi_S \ln \phi_S]$$

Equation 4.6

a simple arithmetic average of the entropies of mixing based upon Raoult's law and the Flory[57]–Huggins[59] model. Equation 4.6 is referred to as the Huyskens and Haulait-Pirson model.[60] The B correction factor is

$$B = 0.5\phi_s(V_A/V_s - 1) + 0.5 \ln[\phi_A + \phi_s(V_A/V_s)]$$ Equation 4.7

Quantities ϕ_A and ϕ_s in eq 4.7 refer to the volume fractions of the dissolved solute and solvent, respectively. Molar volumes, V_A and V_s, used in the volume fraction computations, refer to the pure liquid components. In the case of a crystalline solute, it refers to the hypothetical supercooled solute. The numerical value of V_A can be determined from experimental density for binary solutions containing the solute dissolved in a neat organic solvent. If experimental density data is not available, as is often the case, then the best estimate of the solute molar volume is made by adding up the contributions for each of the functional groups in the molecule. For example, the molecule anthracene would have 10 aromatic CH groups and 4 aromatic carbon atoms.

The justification for using the Huyskens and Haulait–Pirson[60] model for the entropy of mixing can be rationalized as follows. The liquid solution is considered to be an ensemble where the molecules are always moving with respect to each other instead of a deformed lattice. Each molecule of a particular kind has an average volume at its disposal within which to move. This volume is equal to the total volume of the solution divided by the number of molecules of that kind. This mobile domain is not localized or orientable, and it increases as the total volume increases when molecules of another kind are added to the liquid. Given enough time, the molecule not only "visits" all parts of its domain, but it also exchanges its position with that of the foreign molecules occupying the domain. At the border of the domain, the molecule undergoes a series of individual exchanges of places with foreign molecules. The average number is $(x_B)^{1/2} - 1$, as calculated from the random-walk theory of Einstein and Smolukowski.[61]

In a crystal, the entropy of mixing arises from the possibilities of individual exchanges of position in three dimensions. In a gas, the entropy of mixing results from the enlargement of the domain for the motions. Individual exchanges in position can be neglected. For liquids, the entropy of mixing is a hybrid between the entropy of mixing for a crystal and the entropy of mixing for a gas, where the nominal exchanges are ruled by the mole fraction(s), χ, and the enlargements of the domains by the volume fraction(s), ϕ. As a result, the hybrid expression describing the entropy of mixing in liquids is written as[62]

$$\Delta S_{mixing} = -R[n_B \ln(\chi_A^{1/2}\phi_A^{1/2}) + n_S \ln(\chi_S^{1/2}\phi_S^{1/2})] \qquad \text{Equation 4.8}$$

The contribution of the B term is important when the volumes of the solvent, s, and the solute, A, are markedly different from each other. When the volume of the solvent is smaller than that of the solute, the sign of B will be positive resulting in an increase in the solubility.

In eq 4.3, D describes the nonspecific cohesion forces in the solute-solute, solvent-solvent, and solute-solvent interactions in the liquid phase. As a first approximation, the correction factor, D, is calculated

$$D = -\phi_S^2 V_A(\delta_A' - \delta_S')^2/(RT) \qquad \text{Equation 4.9}$$

from an equation of the Scatchard–Hildebrand type[63-66] with adapted solubility parameters ($\delta_A' - \delta_S'$).[67] It is based on the assumption that the solvent-solute cohesive force is equal to the geometric mean of the cohesion energy densities of the two equivalent like pairs, solvent-solvent and solute-solute.

In eq 4.7, the modified solubility parameters account only for nonspecific interactions. In the case of alcohols and self-associating molecules, the hydrogen-bonding contributions have been removed. Ruelle et al.,[49,54] have published compilations of the numerical values of $\delta'_{solvent}$ for a large number of organic molecules. These either were estimated or deduced by regressing the solubility data or solid *n*-alkanes in organic solvents according to the configurational model of Huyskens and Haulait-Pirson.[68] The calculated numerical values of $\delta'_{solvent}$ are affected by any shortcomings of the ability of the Huyskens and Haulait-Pirson model to calculate back to the observed mole fraction solubilities, or any errors or any uncertainties in the measured alkane data.

Examination of eq 4.9 reveals that the contribution of the D term for solvents becomes negligible when the modified solubility parameter of the solvent, δ_s', is close to that of the solutes, δ_A'. Because this contribution is always negative, solubility decreases when δ_A' differs greatly from δ_S'. This endothermic effect explains why the measured solubility of aromatic hydrocarbons in aliphatic alkane or cycloalkane solvents is less than the ideal solubility, based upon eq 4.4.

The relative importance of the melting properties of the solute, the entropy of mixing, and the changes in non-specific forces with respect to solubility have been analyzed by Ruelle et al.[49] They reported that the solubility of solid aromatic hydrocarbons is governed largely by their melting properties. In fact, because the absolute value of A is greater than B and D and is negative in value, it follows that the melting process represents the most important hindrance to the solubility of a solute. In the case of anthracene, where A = –4.544, the energy that must be supplied to lead to the disruption of the crystal is so high that its solubility remains low, twenty-five times lower than that of its isomer phenanthrene (A = –1.507), regardless of the solvent.

Very few systems contain only nonspecific interactions. Most systems of practical importance involve at least some type of specific interaction. For a system such as naphthalene, that is dissolved in a polar self-associating solvent (a proton-donor solvent, such as alcohol), where the hydrogen bonding effects can no longer be ignored, the solubility of the solute expressed by the volume fraction ϕ_A is

$$\phi_A = e^{-A}e^{B}e^{-D}e^{-F}e^{O} \qquad \text{Equation 4.10}$$

F describes the reduction in solubility due to the effect of the hydrogen-bonded chains of the solvent (hydrophobic effect). The alcohol forms linear hydrogen-bonded chains through self-association, and the free hydroxylic OH proton is allowed to interact with the polarizable π-electron cloud of naphthalene. This hydrophobic effect is observed whenever self-associated solvents are considered. It arises from an increase in the temporary loss of freedom of mobility of the solvent molecules when the total volume of the solution is increased by the addition of the solute. For alcohol and water, the hydrophobic effect can be described by

$$F = \phi_S(r_S V_B/V_S) \qquad \text{Equation 4.11}$$

where r_s equals one for monofunctional alcohols; two for water, diols, and other solvents with double chains; and zero for non-associated solvents, such as saturated and aromatic hydrocarbons, ethers, ketones, esters and halogenated derivatives. More exact values for alcoholic solvents can be calculated[54,55] as

$$r_{alco} = (K_{alco}\phi_{alco}/V_{alco})/(1 + K_{alco}\phi_{alco}/V_{alco}) \qquad \text{Equation 4.12}$$

where K_{alco} is the stability constant of the self-association H-bonds. It is called the structuration factor. For primary alcohols at room temperature, K_{alco} is on the order of 5000 cm^3mol^{-1}. For solvents without H-bonding association, e^{-F} is equal to unity. For alcohols and other self-associating solvents, e^{-F} is generally less than one. It is expecially low for water, on the order of 0.0000013. It justifies the name "hydrophobic," according to Ruelle[54] and Huyskens.[60]

According to the Mobile Order theory of Huyskens[30,37,39,60] the hydrophobic effect of alcohols on an inert solute, such as naphthalene, is no longer considered to be a

result of a change in the interaction energies. Rather, it is a result of a lowering of entropy, because of a temporary correlation in the displacements in the liquid of two or more hydroxylic groups of the solvent molecule. As a result, these correlated displacements create a mobile order.

The hydrophobic effect is the reason that naphthalene exhibits lower solubility, both predicted and observed[47] in alcohols with respect to the corresponding nonassociated solvents. Quantitatively, the effect of the F term in eq 4.10 at equilibrium is to reduce solubility in alcohols, ln ϕ_A^{sat}, by an amount equal to $\phi_S V_B/V_S$. Consequently, any increase in the ratio of the molar volumes, V_B/V_S, promotes the solubility of nonpolar substances in nonassociated solvents and disfavors it in alcohols.

From an analysis of the relative importance of the different contributions involved in the solubility calculation, Ruelle et al.[50] reported that the solubility of inert substances in alcohols or water was determined essentially by the hydrophobic effect. This effect corresponds to a decrease of the entropy of the self-associated solvent molecules by the addition of an inert solute. It is seen as a rejection by the solute molecule of the effect of the solvent. In alcohols and water, all or part of the increase in solubility arising from solute-solvent hydrogen bond formation is lost because of the negative hydrophobic effect resulting from solvent self-association, term F.

Many molecules display several sites that are active for H-bonding. Some molecules, such as caffeine, have only proton acceptor sites. Usually, when molecules exhibit proton-donor sites, they also exhibit proton-acceptor sites. When sites of the same nature are connected via delocalized electrons, the competition renders some of

them inactive.[54] The most important acceptor sites are the lone pairs of electrons of the oxygen and nitrogen atoms. The most important proton-donor sites are the OH, SH, and NH hydrogen atoms.

Solvents also may have only acceptor sites. Examples are ketones, esters, ethers, and tertiary amines. However, in general, solvents with donor sites also possess acceptor sites. They are "amphiphilic." Examples of this are water and the alcohols. When dealing with the effects of the H-bonds formed between solute and solvent, it is necessary to treat separately the two kinds of sites. We designate the molecules with the proton acceptor only sites with an "O," and the amphiphilic molecules with "OH."

The O term in eq 4.10 corresponds to

$$O = \ln(1 + K_{Asolv}\phi_{solv}/V_{solv}) \qquad \text{Equation 4.13}$$

where the increase in the solute's volume fraction solubility results from solute-solvent complexation. This complexation is between proton-acceptor sites on the solute and proton-donor solvents. The hydrogen-bond formation is characterized by the K_{Asolv} stability constant of the self-association H-bonds of the solvent. According to the theory of mobile disorder, the ratio $(e^O - 1)/e^O$ is the fraction of time the electron-donor site is involved in H-bonding with the solvent. Ruelle[54] reported that for smaller alcohols and strong electron-donating solutes, this is approximately of 66% of the time. For water, it should be 99%.

When all of the sites of the solute molecule are free, they are still under the influence of the non-specific dipole interactions from the solvent chains. The stabilizing effect decreases when the concentration of the polar groups of the solvent decreases with

dilution, i.e. with the addition of a non-polar solvent. As a result, the constant, K_{Asolv}, will depend on the concentration and nature of these groups.

An additional term is needed in eq 4.10 to describe chemical contributions from both solute self-association and solute-solvent complexation. The solute molecule is amphiphilic, having both proton-donor and proton-acceptor sites. In this case, solute-solvent complexation may involve either a proton-donor or proton-acceptor solvent. The OH chemical contribution

$$OH = -\ln(1 + K_A/V_A) + \ln (K'_{Asolv}\phi_{solv}/V_{solv} + K_A\phi_A^{sat}/V_A)$$

Equation 4.14

depends on the relative strengths of the different molecular interactions. It describes the positive effect of the temporary hydrogen bond involving the acidic alcoholic proton.

In the frame of thermodynamics of the mobile order at saturation equilibrium, the general solubility equation may contain as many as six terms. A direct physical interpretation can be written[56] as

$$\ln \phi_B = - A + B - D - F + O - OH \qquad \text{Equation 4.15}$$

The general predictive expression, as given by eq 4.15, contains terms describing the breaking of solute-solute interactions in the crystalline lattice (A), solvent self-association (F), solute self-association (OH), solute-solvent complexation for hydrogen-bond formation involving either the solute OH or solvent OH functional group(s) (OH), and nonspecific solute-solvent interactions (D). Not all systems encountered will require all six terms. The actual number of terms needed will be determined by the functional groups present on the solute and solvent molecules. For example, in the case of a liquid

solute, term A equals zero, as no energy is expended to break the crystalline lattice. In the case when all six terms equal zero, ϕ_B is equal to one. That means B would be miscible in all proportions of the solvent.

Mobile order theory is successful because of the correct description of the entropic and hydrophobic effects. Alcohols will never form the "regular solutions." The deviations are due exclusively to energistic effects. The premise that regular solution theory does not predict solubilities correctly is the basis of the Mobile Order Theory preferred by Huyskens.[28,29,32,34,40,60]

Mobile Order Theory in Binary Solvent Systems

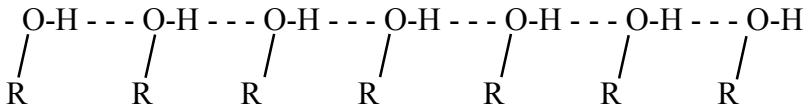
This dissertation continues a systematic search for simple mixing models that will provide reasonable mathematical descriptions of the thermodynamic properties of nonelectrolyte solutions. Solutions that contain components capable of self-association are of particular interest. To date, both the applications and limitations of mobile order theory have been examined regarding the description of the solubility of anthracene in 34 different binary alkane + alcohol,[13,69-72] 57 binary alcohol + alcohol,[73-77] 50 alcohol + alkoxyalcohol,[62,78,79] and 34 alkane + alkoxyalcohol,[80,81] and of pyrene dissolved in 42 different binary alcohol + alcohol[62,82,83] and 27 binary alkane + alcohol[72] solvent mixtures. The derived expressions predicted the experimental mole fraction solubilities to within an overall average absolute deviation of less than 4.5%. This was achieved by using a single numerical value of $K_{alcohol} = 5{,}000$ cm^3 mol^{-1} for the association constant of the nine monofunctional alcohol and five alkoxyalcohol cosolvents which were studied.

Nonspecific interactions were expressed in terms of modified solubility parameters. In mixtures containing two alcohol cosolvents, the thermodynamic treatment included the formation of both homogeneous and heterogeneous cross-associated hydrogen-bonded chains. The two polycyclic self-associated aromatic hydrocarbons (PAHs) were treated initially as inert solutes incapable of forming molecular complexes with any of the alcohol cosolvents present. The inclusion of a single PAH-alcohol association complex significantly improved the predictive accuracy of the derived expressions.[72]

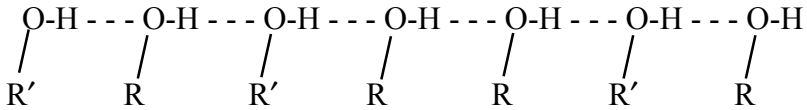
These earlier studies briefly looked at the ability of mobile order theory and the Kretschmer–Wiebe stepwise self-association model to mathematically represent vapor-liquid equilibria (VLE) data for binary alkane + alcohol systems. For each model, alcohol-specific association constants and binary interaction parameters were calculated from binary VLE data. They were used then in anthracene solubility predictions. Both solution models produced reasonable results. The Kretschmer–Wiebe model did provide a slightly better mathematical description of the experimental values for the 20 systems for which both VLE and anthracene solubility data could be found. Overall root mean square deviations for the VLE representation were 0.13 and 0.19 kPa for the Kretschmer–Wiebe model and mobile order theory, respectively. Anthracene was considered to be an inert solute in all calculations involving the Kretschmer–Wiebe model. This assumption greatly simplified the computations, particularly in the solvent systems containing two alcohol cosolvents. In this case, a reiterative method was required to calculate the concentrations of the alcohol monomers.

Mobile Order Theory in Ternary Solvent Systems

In this dissertation, I am extending Mobile Order theory to ternary solvent mixtures. Expressions are derived for predicting the solubility of crystalline polycyclic aromatic hydrocarbon solutes dissolved in a ternary alcohol (B) + alcohol (C) + alkane (D) and alcohol + alcohol + alcohol solvent mixtures. Such mixtures are characterized by both the presence of long homogeneous H-bonded chains of the type



caused by self-association of the two alcohol cosolvents, and also by the chains



involving hydrogen-bonding between dissimilar alcohol molecules.

Application and limitation of the newly-derived equation(s) are illustrated by using published anthracene solubility in twelve different ternary propanol + butanol + alkane[6-8], four ternary 2-alkoxyalcohol + alcohol + alkane, four ternary alcohol + alcohol + alcohol, eight ternary propanol (or butanol) + alkane + alkane[4,5], and four alkoxyalcohol + alkane + alkane solvent mixtures. The alkane cosolvents that were studied are heptane, cyclohexane and 2,2,4-trimethylpentane. Predictions for the latter twelve ternary solvent systems were achieved by setting the two cross-association stability constants (K_{BC} and K_{CB}) and self-association constant of solvent component C (K_C) equal to zero.

Development of Predictive Expression for Inert Solutes In Ternary Solvent Systems Containing Two Alcohol Cosolvents

Essential features of Mobile Order theory, as they pertain to a quaternary mixture containing an inert solute (component A), two alcohol cosolvents (components B and C) and an alkane cosolvent (component D), will be reviewed briefly to facilitate development of the final derived equations(s). The Gibbs energy of mixing for the quaternary solution is separated into three contributions:

$$\Delta G_{ABCD}^{mix} = (\Delta G_{ABCD})_{conf} + (\Delta G_{ABCD})_{chem} + (\Delta G_{ABCD})_{phys}$$

Equation 4.16

The first term describes the configurational entropy based upon the Huyskens and Haulait-Pirson[84] definition of solution ideality

$$(\Delta G_{ABCD})_{conf} = (0.5)RT *$$

$$[n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln \phi_C + n_D \ln \phi_D + n_A \ln \chi_A + n_B \ln \chi_B + n_C \ln \chi_C + n_D \ln \chi_D]$$

Equation 4.17

The last two terms in eq 4.16 result from the formation of hydrogen-bonded complexes and weak nonspecific interactions in the quaternary solution, respectively.

The chemical contribution depends upon the functional groups present and the characteristics of the self-associating component. Alcohols have one hydrogen "donor" site, and the two lone electron pairs on the oxygen atom provide two "acceptor" sites. The maximum possible number of hydrogen bonds is determined by the number of sites that are in a minority. Monofunctional alcohols do form self-associated species. There is no prior experimental evidence or computational reason to preclude formation of

heterogeneous B_iC_j complexes, especially if we are using a single equilibrium constant to describe every monofunctional alcohol's self-association characteristics. For each alcohol, the fraction of time that the alcohol is not involved in hydrogen-bond formation is

$$\gamma_{Bh:} = 1/[1 + K_B (\phi_B/V_B) + K_{BC} (\phi_C/V_C)] \qquad \text{Equation 4.18}$$

and

$$\gamma_{Ch:} = 1/[1 + K_{CB} (\phi_B/V_B) + K_C (\phi_C/V_C)] \qquad \text{Equation 4.19}$$

where K_{BC} and K_{CB} refer to the two additional equilibrium constants needed to describe the formation of the new heterogeneous alcohol-alcohol complexes not found in either neat solvent. It readily can be shown that this set of conditions leads to the following expressions for the Gibbs energy for the hydrogen-bonding contribution

$$(\Delta G_{ABCD})_{chem} = n_B RT \ln[(1 + K_B/V_B)/(1 + K_B (\phi_B/V_B) + K_{BC} (\phi_C/V_C))] +$$

$$n_C RT \ln[(1 + K_C/V_C)/(1 + K_{CB} (\phi_B/V_B) + K_C (\phi_C/V_C))]$$

Equation 4.20

Physical nonspecific interactions are expressed in terms of the Scatchard–Hildebrand solubility parameter type model

$$(\Delta G_{ABCD})_{phys} = (n_A V_A + n_B V_B + n_C V_C + n_D V_D)[\phi_A\phi_B(\delta_A' - \delta_B')^2 + \phi_A\phi_C(\delta_A' - \delta_C')^2 +$$

$$\phi_A\phi_D(\delta_A' - \delta_D')^2 + \phi_B\phi_C(\delta_B' - \delta_C')^2 + \phi_B\phi_D(\delta_B' - \delta_D')^2 + \phi_C\phi_D(\delta_C' - \delta_D')^2]$$

Equation 4.21

As stated previously, modified solubility parameters, δ_i', account only for nonspecific interactions. In the case of the two alcohol solvents, the hydrogen-bonding contributions

are removed. Numerical values of δ_i' are available in several published compilations.[47,49,54]

It is noted that other research groups have treated nonspecific interactions differently. They assumed solution models other than the Scatchard–Hildebrand solubility parameter theory. For example, Ruelle,[42] in predicting solubilities in systems involving hydrogen-bond formation between a dissolved solute and surrounding solvent molecules, modified the Scatchard–Hildebrand expression by multiplying it by the fraction of time during which the solute is not bound to the solvent (i.e., during which the distribution between the solvent and unbound solute molecules still can be considered to occur at random). Ruelle's treatment also assumed that nonspecific interactions involving the bound solute were negligible. The theoretical justification for Ruelle's modification was not given. It is not clear what mathematical form the integral $(\Delta G_{AB})_{phys}$ for the binary solution would have to take in order to give

$$(\Delta G_{AB})_{phys} = \{1/[1.0 + \max(K_{O_i}, K_{OH_i})(\phi_{solv}/V_{solv})]\} \times \phi_{solv}^2 V_A(\delta_A' - \delta_{solv}')^2$$

Equation 4.22

whenever $(\Delta G_{AB})_{phys}$ is differentiated with respect to the number of moles of solute which are present. This differentiation is required in deriving the solubility equation. It also should be noted that any modification in the $(\Delta G_{AB})_{phys}$ expression must also appear in the corresponding $(\Delta G_B)_{phys}$ expression. The latter expression is obtained by differentiating $(\Delta G_{AB})_{phys}$ with respect to the number of moles of solvent. In eq 4.22

$\max(K_{O_i}, K_{OH_i})$ stands for the association constant governing the strongest intermolecular H-bond displayed by the molecular groups in solution.

I have chosen to use the Scatchard–Hildebrand solubility parameter theory, eq 4.21, rather than the Ruelle modification, because of serious concerns about how to express mathematically the $(\Delta G_{ABCD})_{phys}$ contribution for the time that alcohol B is not bound to alcohol C, and for the time that alcohol C is not bound to alcohol B. Moreover, serious reservations exist about whether nonspecific interactions for bound molecules are truly negligible, as assumed by Ruelle in proposing eq 4.22. By combining eqs 4.16, 4.17, 4.20, and 4.21, the Gibbs energy of mixing (per stoichiometric mole of mixing) is written as

$$\Delta G_{ABCD}^{mix} = (0.5)RT \times [n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln \phi_C + n_D \ln \phi_D + n_A \ln \chi_A + n_B \ln \chi_B + n_C \ln \chi_C + n_D \ln \chi_D] + n_B RT \ln[(1 + K_B/V_B)/(1 + K_B (\phi_B/V_B) + K_{BC}(\phi_C/V_C))] + n_C RT \ln[(1 + K_C/V_C)/(1 + K_{CB} (\phi_B/V_B) + K_C (\phi_C/V_C))] + (n_A V_A + n_B V_B + n_C V_C + n_D V_D)[\phi_A\phi_B(\delta_A' - \delta_B')^2 + \phi_A\phi_C(\delta_A' - \delta_C')^2 + \phi_A\phi_D(\delta_A' - \delta_D')^2 + \phi_B\phi_C(\delta_B' - \delta_C')^2 + \phi_B\phi_D(\delta_B' - \delta_D')^2 + \phi_C\phi_D(\delta_C' - \delta_D')^2] \quad \text{Equation 4.23}$$

Thermodynamic principles relate solubility to chemical potential. For a system obeying eq 4.21, the volume fraction solubility, ϕ_A^{sat}, of a sparingly soluble solute, ($\phi_A^{sat} \approx 0$), is

$$RT \ln a_A^{solid} = RT\{ \ln \phi_A^{sat} + 0.5[1 - V_A/(\chi_B^{\circ} V_B + \chi_C^{\circ} V_C + \chi_D^{\circ} V_D)] - 0.5 \ln[V_A/(\chi_B^{\circ} V_B + \chi_C^{\circ} V_C + \chi_D^{\circ} V_D)] + (V_A/V_B)RT\phi_B^{\circ}[\phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)]/[1 + \phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)] + (V_A/V_C)RT\phi_C^{\circ}[\phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)]/[1 + \phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)] + V_A[\phi_B^{\circ}(\delta_A' - \delta_B')^2 + \phi_C^{\circ}(\delta_A' - \delta_C')^2 +$$

$$\phi_D^{\circ}(\delta_A' - \delta_D')^2 - \phi_B^{\circ}\phi_C^{\circ}(\delta_B' - \delta_C')^2 - \phi_B^{\circ}\phi_D^{\circ}(\delta_B' - \delta_D')^2 - \phi_C^{\circ}\phi_D^{\circ}(\delta_C' - \delta_D')^2]$$

Equation 4.24

obtained by differentiating eq 4.23 with respect to the number of moles of the solute. In eq 4.24, χ_i° and ϕ_i° denote the mole fraction and volume fraction composition of component *i* in the initial ternary solvent mixture, which is calculated as if the solute were not present. V_i is the molar volume of component *i*, and a_A^{solid} is the activity of the solid solute. This latter quantity is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical subcooled liquid. The numerical value of a_A^{solid} can be computed from the solute's molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature, T_{mp} (see eq. 4.4).

A close look at the above expression reveals that it is possible to eliminate the three terms involving the modified solubility parameter of the solute using

$$V_A(\delta_A' - \delta_B')^2 = RT\{\ln[a_A^{solid}/(\phi_A^{sat})_B] - 0.5(1 - V_A/V_B) + 0.5\ln(V_A/V_B)\} - RT(V_A/V_B)(K_B/V_B)/[1 + (K_B/V_B)]$$

Equation 4.25

$$V_A(\delta_A' - \delta_C')^2 = RT\{\ln[a_A^{solid}/(\phi_A^{sat})_C] - 0.5(1 - V_A/V_C) + 0.5\ln(V_A/V_C)\} - RT(V_A/V_C)(K_C/V_C)/[1 + (K_C/V_C)]$$

Equation 4.26

and

$$V_A(\delta_A' - \delta_D')^2 = RT\{\ln[a_A^{solid}/(\phi_A^{sat})_D] - 0.5(1 - V_A/V_D) + 0.5\ln(V_A/V_D)\}$$

Equation 4.27

the measured volume fraction solubilities in the pure solvents, $(\phi_A^{sat})_B$, $(\phi_A^{sat})_C$, and $(\phi_A^{sat})_D$. Substitution of eqs 4.24 – 4.26 into eq 4.23, followed by suitable algebraic manipulations, yields the following expression

$$\ln \phi_A^{sat} = \phi_B^{\circ} \ln(\phi_A^{sat})_B + \phi_C^{\circ} \ln(\phi_A^{sat})_C + \phi_D^{\circ} \ln(\phi_A^{sat})_D -$$

$$0.5[\ln(\chi_B^{\circ} V_B + \chi_C^{\circ} V_C + \chi_D^{\circ} V_D) - \phi_B^{\circ} \ln V_B - \phi_C^{\circ} \ln V_C - \phi_D^{\circ} \ln V_D] -$$

$$(V_A/V_B)\phi_B^{\circ}[\phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)]/[1 + \phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)] +$$

$$(V_A K_B \phi_B^{\circ}/V_B^2)(1 + K_B/V_B)^{-1} - (V_A/V_C)\phi_C^{\circ}[\phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)] /$$

$$[1 + \phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)] + (V_A K_C \phi_C^{\circ}/V_C^2)(1 + K_C/V_C)^{-1} +$$

$$[\phi_B^{\circ}\phi_C^{\circ}(\delta_B' - \delta_C')^2 + \phi_B^{\circ}\phi_D^{\circ}(\delta_B' - \delta_D')^2 + \phi_C^{\circ}\phi_D^{\circ}(\delta_C' - \delta_D')^2]V_A(RT)^{-1}$$

Equation 4.28

for the solubility of an inert solute in a ternary alcohol + alcohol + alkane solvent mixture. Note that a_A^{solid} was eliminated mathematically from the final derived expression, a consequence of replacing the three terms involving the solute's modified solubility parameter with the measured solute solubilities in pure solvents B, C. and D. Elimination of the a_A^{solid} term from the predictive equation can lead to better solubility estimates, particularly in the case of high melting point solutes. Equation 4.5 is only an approximate expression. Two additional terms involving differences between the molar heat capacities of the liquid and solid, ΔC_p, were dropped from the more rigorous a_A^{solid} computation (see eq 4.4). This is because ΔC_p data is not available generally in the chemical literature for high melting point solutes such as anthracene.

Mobile Order Theory Solubility Predictions for Inert Solutes

Despite the complex appearance of eq 4.28, its application to solubilities in ternary alcohol + alcohol + alkane and ternary alcohol + alkane + alkane solvent mixtures

is relatively straightforward. It is also similar to numerical examples presented previously[85]. The quantities $(\phi_A^{sat})_B$, $(\phi_A^{sat})_C$, and $(\phi_A^{sat})_D$ are calculated from measured mole fraction solubilities of the solid in the pure solvents, assuming that the excess molar volume (or alternatively the volume change upon mixing) is zero. These three quantities, along with the molar volumes, modified solubility parameters, numerical values of the equilibrium constants for formation of homogeneous (K_B and K_C), and heterogeneous (K_{BC} and K_{CB}) hydrogen-bonded chains, are inserted then into eq 4.28 to calculate ϕ_A^{sat} at each ternary solvent composition. Equation 4.28 assumes that the two alcohol cosolvents undergo both self-association and cross-association. The formation of cross-associated B_iC_j species can be eliminated from the model simply by setting the two cross-association stability constants, K_{BC} and K_{CB}, equal to zero. Our prior studies have shown that when anthracene and pyrene are dissolved in binary alkane + alcohol and alcohol + alcohol solvent mixtures, the Mobile Order theory provided very reasonable predictions, assuming identical numerical values of $K_B = K_C = K_{BC} = K_{CB} = 5{,}000$ cm^3 mol^{-1} for the homogeneous and heterogeneous stability constants for all monofunctional alcohols.

The predictive ability of eq 4.28 is summarized in the middle column of Table II for anthracene dissolved in twelve different ternary propanol + butanol + alkane[6-8] and eight ternary propanol (or butanol) + alkane + alkane[4,5,84] solvent mixtures. Predictions for the latter eight ternary solvent systems were achieved by setting the two cross-association stability constants (K_{BC} and K_{CB}) and self-association constant of solvent component C (K_C) equal to zero. Each system contained solubility data at nineteen different ternary compositions spanning the entire mole fraction range, as well as

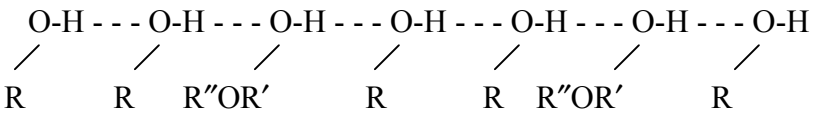
measured anthracene solubility in the three pure solvents. The measured mole fraction solubilities were based upon 4–8 replicate measurements. They were reproducible to within ± 1.5%. The solvent molar volumes and the modified solubility parameters used in the Mobile Order theory computations are listed in Table III. The molar volume of the subcooled anthracene solute is approximated as $V_A = 150$ cm^3 mol^{-1}. An uncertainty of ± 10% in the numerical value assumed for V_A contributes very little error to the overall solubility predictions.

Examination of the numerical entries in the middle column of Table II reveals the Mobile Order theory predictions and the mole fraction solubility of anthracene fall within an overall average absolute deviation of ± 5.8%. Readers are reminded that eq 4.28 does require the experimental mole fraction solubilities in the three pure solvents as input values. The imputed $(\phi_A^{sat})_i$ values do have ± 1.5% uncertainties associated with them. Error propagation analysis, assigning reasonable uncertainties to all the input values, gives a calculational uncertainty of about ± 2.5% to each predicted ϕ_A^{sat} value. The propagated uncertainty is slightly less than half of the average absolute deviation between the predicted and observed values.

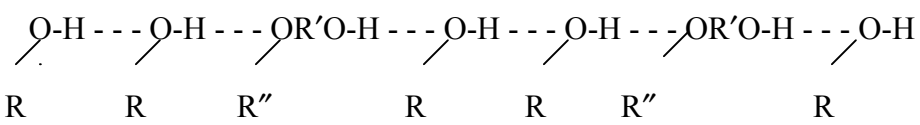
The Mobile Order theory predictions (though by no means perfect) agree with earlier experiences using this particular solution model. As stated at the beginning of this subsection, past studies have shown that Mobile Order theory describes the solubility of anthracene in 34 different binary alkane + alcohol,[13,69-72] 57 binary alcohol + alcohol,[73-77] 50 alcohol + alkoxyalcohol,[62,78,79] 34 alkane + alkoxyalcohol,[81] and of

pyrene dissolved in 42 different binary alcohol + alcohol[62,82,83] and 27 binary alkane + alcohol[72] solvent mixtures to within an overall average absolute deviation of less than 4.5%, using a single numerical value of $K_{alcohol}$ = 5,000 cm^3 mol^{-1} for the association constant of the nine monofunctional alcohol and five alkoxyalcohol cosolvents which were studied. Of all the binary systems previously studied, deviations between predicted and observed anthracene solubilities were largest in solvent mixtures containing both an alkane and alcohol cosolvent. The binary alkane + alcohol solvent mixtures covered the larger range of anthracene mole fraction solubilities. The predictive accuracy of most solution models does decrease with increasing solution nonideality and with greater dissimilarities between the solute solubility in the pure solvents. A fair comparison would be to compare the ternary solvent predictions to those involving anthracene dissolved in binary alkane + alcohol solvent mixtures. They cover comparable ranges in mole fraction solubilities. Mobile Order theory predicted the solubility behavior of anthracene in binary alkane + alcohol solvent mixtures to within an average absolute deviation of ± 5.7%. [69,70] Statistically, there is no difference in the predictive ability of Mobile Order theory when used to predict anthracene solubilities in binary and ternary solvent mixtures containing both an alkane and alcohol cosolvent. Based upon the comparisons presented above, I conclude that there is no loss in predictive ability in extending Mobile Order theory to higher-order multicomponent solvent mixtures.

McHale et al.[78] investigated the ability of Mobile Order theory to predict the solubility of anthracene in binary alcohol + alkoxyalcohol solvent mixtures. Such mixtures are characterized by both the presence of long H-bonded chains of the type



wherein hydrogen-bonding occurs through the hydroxyl group, and also by the chains



that hydrogen-bond through the ether linkage. From the point-of-view of Mobile Order theory, both scenarios lead to extension of the H-bonded chain. McHale et al. investigated the possibility of treating the alkoxyalcohol as a "pseudo" mono-functional alcohol cosolvent. An alkoxyalcohol possesses an ether oxygen atom in addition to the alcoholic OH functional group. In molecules where the ether oxygen atom is present, one generally finds a significant increase in the numerical value of the modified solubility parameter relative to that of the *n*-alkane homolog (i. e., $\delta_{solv}' = 17.96$ MPa$^{1/2}$ for dipropyl ether vs. $\delta_{solv}' = 14.56$ MPa$^{1/2}$ for *n*-hexane). This suggests that the significant solubility enhancement noted in the 2-alkoxy-ethanol solvents results largely from differences in nonspecific interactions, as contrasted to differences in the hydrogen-bonding characteristics of the two solvent types.

While investigating the solubility of anthracene in binary solvent systems of alcohol + alkoxyalcohol, McHale et al.[78] considered the possibility of not only homogeneous self-associated hydrogen bonds with the surrounding molecules of the same type, but also the formation of heterogeneous hydrogen bonds between the alcohol and alkoxyethanol molecules. They showed that the equation for the saturation solubility of a sparingly soluble solute dissolved in the binary alcohol + alkoxyethanol solvent

mixture is identical to the Mobile Order theory equation for a binary alcohol + alcohol solvent mixture, with the only difference being that the stability constants for the alkoxyalcohols may be slightly larger than 5,000, because of the hydrogen bonding site furnished by the two lone electron pairs on the ether oxygen atom. While the authors noted that the additional hydrogen bond site might increase the stability constant up to 5,200, they assumed a value of 5,000 for all monofunctional alcohols and alkoxyalcohols for calculational simplicity. The assumption simplified the treatment of hydrogen bonds found between the alcohol and alkoxyalcohol solvent molecules.

McHale et al. concluded that an equation assuming the formation of homogeneous hydrogen-bonded alcohol chains plus heterogeneous alcohol + 2-alkoxyalcohol chains is slightly better than an equation that just considers only the formation of homogeneous hydrogen-bonded alcohol chains. It provided an overall average deviation between measured and calculated values at 2.5%. Hernández et al.[86] subsequently used Mobile Order theory to describe the solubility behavior of anthracene in 34 different binary alkane + alkoxyalcohol solvent mixtures. Mobile Order theory was found to predict the published anthracene solubility data to within an overall average deviation of approximately ± 5.0%.

It should be noted that in applying Mobile Order theory to binary alkoxyalcohol + alcohol solvent mixtures, McHale et al.[78] did require numerical values for the modified solubility parameters of the four 2-alkoxyalcohols (2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, and 2-butoxyethanol) studied. Published compilations did not list numerical values of δ_i' for alkoxyalcohols. McHale et al. argued that the modified

solubility parameters of alkoxyalcohols should exceed the tabulated values of the corresponding alcohols of comparable molecular size. An alkoxyalcohol possesses an ether oxygen atom in addition to the alcoholic OH functional groups. In ether molecules where the oxygen atom is present, there is a significant increase in the numerical value of δ_i' relative to the n-alkane homolog. For example, the modified solubility parameter of $\delta_i' = 17.96$ mPa$^{1/2}$ for dipropyl ether is significantly larger than $\delta_i' = 14.56$ mPa$^{1/2}$ for n-hexane. The effect does level off with increasing alkyl chain length (i.e., $\delta_i' = 16.16$ mPa$^{1/2}$ for dipentyl ether versus $\delta_i' = 15.14$ mPa$^{1/2}$ for n-decane). Based upon these observations, the authors estimated the solubility parameters of 2-methoxyethanol as $\delta_i' =$ 20.8 mPa$^{1/2}$, of 2-ethoxyethanol as $\delta_i' = 20.3$ mPa$^{1/2}$, of 2-propoxyethanol as $\delta_i' = 19.8$ mPa$^{1/2}$, and of 2-butoxyethanol as $\delta_i' = 19.2$ mPa$^{1/2}$.

The modified solubility parameters for the alkoxyalcohols do have uncertainties/errors associated with their estimated numerical values. Careful examination of the $V_A\phi_B^\circ\phi_C^\circ(\delta_B' - \delta_C')^2(RT)^{-1}$ term in eq 4.28 reveals that its contributions to the predicted solute solubility becomes increasingly larger as the difference in δ_B' and δ_C' increases. From a mathematical point-of-view, this translates to the following observation. The estimated modified solubility parameters of the alkoxyalcohols are closer to the δ_i' values of alcohols than to the δ_i' values of alkanes. Errors/uncertainties in the δ_i' values of alkoxyalcohols affect the predicted solubilities more in the case of binary alkane + alkoxyalcohol solvent mixtures, than in the case of binary alcohol + alkoxyalcohol solvent mixtures. This may explain in part why the

deviations between the observed and predicted solubilities were larger in the study of Hernández et al.[86] compared to the study of McHale et al.[78]

This dissertation extends Mobile Order theory to ternary solvent systems consisting of an alkoxyalcohol + alkane + alkane, alkoxyalcohol + alcohol + alkane, and alkoyxalcohol + alcohol + alcohol. Application and limitation of eq 4.28 was assessed using published anthracene solubilities.[9-11] As shown in the middle column of Table VI, the overall average absolute deviation for the four 2-alkoxyalcohol + alkane + alkane systems was 5.84%. The middle column of Table VII gives an overall average absolute deviation of 4.62 % for the four 2-alkoxyalcohol + alcohol + alkane systems studied. This compares favorably to the study by Hernández[86] et al. for thirty-four binary alkane + alkoxyalcohol solvent mixtures. They found that Mobile Order theory predicted the observed anthracene solubility to within an overall absolute deviation of *circa* ± 5.0%. Based upon the above observations, I concluded that very little, if any, predictive accuracy was lost in extending Mobile Order theory to ternary alcohol + alkoxyalcohol + alkane and alkoxyalcohol + alkane + alkane solvent mixtures.

Extension of Mobile Order Theory to Include Solute-Alcohol Complexation

The thermodynamic treatment, thus far, has assumed that anthracene is an inert solute. It may be possible to improve the predictive ability of Mobile Order theory by including solute-solvent association terms into the basic model. Complexation involving a polycyclic aromatic hydrocarbon's (PAHs) polarizable π-electron cloud and the

alcohol's OH functional group is not unreasonable. In fact, published vapor-liquid and liquid-liquid equilibria ,[87-93] calorimetric,[94,95] and spectroscopic[96,97] data are frequently interpreted with theoretical models that assume formation of a PAH-alcohol complex. Moreover, Ruelle et al.[98] assumed a weak PAH-water complex in rationalizing the aqueous solubility behavior of crystalline polycyclic aromatic hydrocarbons. The calculated stability constant, although very small ($K_{complex} \approx 80$ cm^3 mol^{-1}), did have an appreciable effect in terms of explaining the enhanced PAH solubilities. Without the complexation term, Mobile Order theory predictions for the PAH solutes were systematically low. Ruelle and Kesselring[99] also used Mobile Order theory to predict aqueous solubilities of proton-acceptor oxygen-containing solutes. Again, this author assumed a numerical value of $K_{complex} \approx 80$ cm^3 mol^{-1} for the stability constant for water's OH functional group interacting with a fused aromatic ring.

Extension of eq 4.28 to systems containing both AB and AC molecular complexation is relatively straightforward. Three terms are added to the final derived equation

$$\ln \phi_A^{sat} = \phi_B^\circ \ln(\phi_A^{sat})_B + \phi_C^\circ \ln(\phi_A^{sat})_C + \phi_D^\circ \ln(\phi_A^{sat})_D -$$

$$0.5[\ln(\chi_B^\circ V_B + \chi_C^\circ V_C + \chi_D^\circ V_D) - \phi_B^\circ \ln V_B - \phi_C^\circ \ln V_C - \phi_D^\circ \ln V_D] +$$

$$\ln[1 + \phi_B^\circ K_{AB}/V_B + \phi_C^\circ K_{AC}/V_C] - \phi_B^\circ \ln [1 + K_{AB}/V_B] - \phi_C^\circ \ln [1 + K_{AC}/V_C] -$$

$$(V_A/V_B)\phi_B^\circ[\phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)]/[1 + \phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)] +$$

$$(V_A K_B \phi_B^\circ/V_B^2)(1 + K_B/V_B)^{-1} - (V_A/V_C)\phi_C^\circ[\phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)] /[1 +$$

$$\phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)] + (V_A K_C \phi_C^\circ/V_C^2)(1 + K_C/V_C)^{-1} +$$

$$[\phi_B{}^{\circ}\phi_C{}^{\circ}(\delta_B' - \delta_C')^2 + \phi_B{}^{\circ}\phi_D{}^{\circ}(\delta_B' - \delta_D')^2 + \phi_C{}^{\circ}\phi_D{}^{\circ}(\delta_C' - \delta_D')^2]V_A(RT)^{-1}$$

Equation 4.29

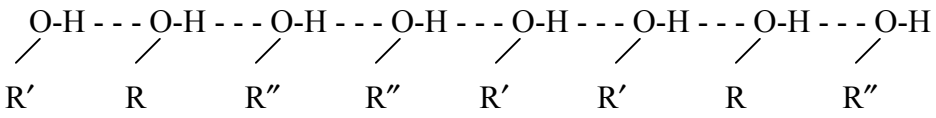
to describe complexation in the ternary solvent mixture, the $\ln[1 + \phi_B{}^{\circ}K_{AB}/V_B + \phi_C{}^{\circ}K_{AC}/V_C]$ term, and in the two pure alcohol cosolvents, the $\phi_B{}^{\circ} \ln [1 + K_{AB}/V_B] - \phi_C{}^{\circ} \ln [1 + K_{AC}/V_C]$ terms. The latter two terms are introduced whenever the $\phi_B{}^{\circ}V_A(\delta_A' - \delta_B')^2$ and $\phi_C{}^{\circ}V_A(\delta_A' - \delta_C')^2$ nonspecific interactions are eliminated from the basic model in favor of the measured PAH solute solubilities in the pure alcohol cosolvents. As before, the final derived expression applies to solutes of limited solubilities, (*i.e.*, $\phi_A{}^{sat} \approx 0$). Equation 4.29 can be used to predict anthracene solubilities in ternary alcohol + alkane + alkane solvent mixtures by setting all stability constants involving component C (K_C, K_{BC}, K_{CB}, and K_{AC}) equal to zero.

Predictive application of eq 4.29 requires a priori knowledge of the numerical value for a given PAH-alcohol stability constant. In principle, one could have a different numerical value for each alcohol cosolvent. Such approaches would restrict predictions to alcohols already studied. They also would represent more of a "curve-fitting" exercise, rather than an outright solubility prediction. To maintain as much generality as possible, we elected to define a single stability constant for all four anthracene-alcohol complexes. The stability constant is, thus, independent of the alcohol cosolvent. This assumption seems reasonable in that only monofunctional alcohols were studied in the present investigation, and the molecular size of the single OH functional group (H-bond donor site) is approximately the same for linear and branched alcohols. Based upon eight sample computations, it was decided to use a numerical value of $K_{AB} = K_{AC} = 125$ cm^3

mol^{-1} for the presumed anthracene-alcohol complexes. This value accurately reproduced the observed anthracene data in our set of preliminary computations. Table IV examines the change in the average per cent deviation between predicted vs. measured solubilities as a function of K_{AB} changes. In each case, the value for K_{AB} giving the lowest average per cent deviation falls in the range 80–215 cm^3 mol^{-1}. Using these minima in the average per cent deviation calculations changed the predicted values by less than 1%. Since the desire was to develop an outright solubility prediction, setting K_{AB} = 125 cm^3 mol^{-1} is a valid assumption. The last column of Table II compares the predictions of eq 4.29 to the experimental anthracene solubility data. Examination of the numerical entries reveals that deviations between the observed and predicted values does decrease whenever the model includes the formation of an anthracene-alcohol complex. The overall average deviation went from approximately ± 5.8% to ± 4.5% for the ternary solvent mixtures which were examined.

Extension of Mobile Order Theory for Alcohol + Alcohol + Alcohol Ternary Solvent Systems

The success of Mobile Order theory in describing the solubility behavior of anthracene dissolved in both ternary alcohol + alcohol + alkane and ternary alcohol + alkoxyalcohol + alkane solvent mixtures suggests that the basic model might provide a reasonably accurate thermodynamic description for ternary solvent mixtures containing three alcohol cosolvents. The idea is certainly worth pursuing. Such mixtures are characterized by heterogeneous hydrogen-bonded chains of the type



Predictive expressions for solute solubility in ternary alcohol + alcohol + alcohol solvent mixtures can be rigorously derived by writing the configurational, chemical, and physical contributions to the Gibbs energy of mixing, and then differentiating the total Gibbs energy of mixing with respect to the number of moles of solute, as was done in deriving eq 4.24. The three terms involving the modified solubility parameter of the solute could then be eliminated from the derivative equation using the measured volume fractions solubilities in the pure solvents. The mathematical details would be essentially identical to those given in the section titled "Development of Predictive Expression for Inert Solutes in Ternary Solvent Systems Containing Two Alcohol Cosolvents."

An alternative method for arriving at the final predictive expression would be to carefully compare the predictive equations for a solute dissolved in a binary alcohol (B) + alkane (C) solvent mixture (i.e., eq 4.28 with $\phi_D^\circ = 0$, $\chi_D = 0$ and $K_{BC} = K_{CB} = K_C = 0$)

$$\ln \phi_A^{sat} = \phi_B^\circ \ln(\phi_A^{sat})_B + \phi_C^\circ \ln(\phi_A^{sat})_C -$$

$$[\ln(\chi_B^\circ V_B + \chi_C^\circ V_C) - \phi_B^\circ \ln V_B - \phi_C^\circ \ln V_C] -$$

$$(V_A/V_B)\phi_B^\circ\phi_B^\circ(K_B/V_B)/[1 + \phi_B^\circ(K_B/V_B)] +$$

$$(V_A K_B \phi_B^\circ/V_B^2)(1 + K_B/V_B)^{-1} + \phi_B\phi_C(\delta_B' - \delta_C)^2 V_A(RT)^{-1}$$

Equation 4.30

and for a solute dissolved in a binary alcohol (B) + alcohol (C) solvent mixture (i.e., eq 4.28 with $\phi_D^\circ = 0$ and χ_B°)

$$\ln \phi_A^{sat} = \phi_B^\circ \ln(\phi_A^{sat})_B + \phi_C^\circ \ln(\phi_A^{sat})_C -$$

$$[\ln(\chi_B^\circ V_B + \chi_C^\circ V_C) - \phi_B^\circ \ln V_B - \phi_C^\circ \ln V_C] -$$

$$(V_A/V_B)\phi_B^\circ[\phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)]/[1 + \phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)] +$$

$$(V_A K_B \phi_B^\circ/V_B^2)(1 + K_B/V_B)^{-1} -$$

$$(V_A/V_C)\phi_C^\circ[\phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)]/[1 + \phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)] +$$

$$(V_A K_C \phi_C^\circ/V_C^2)(1 + K_C/V_C)^{-1} +$$

$$\phi_B^\circ \phi_C^\circ(\delta_B' - \delta_C')^2 V_A(RT)^{-1} \qquad \text{Equation 4.31}$$

to see what changes were required in replacing the alkane cosolvent with an alcohol cosolvent. The changes involved extending alcohol B's hydrogen-bonding term to include the possibility of forming heterogeneous hydrogen-bonded chains

$$(V_A/V_B)\phi_B^\circ\phi_B^\circ(K_B/V_B)/[1 + \phi_B(K_B/V_B)] \square$$

$$(V_A/V_B)\phi_B^\circ[\phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)]/[1 + \phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C)]$$

and adding two terms to describe the hydrogen-bonding of the second alcohol cosolvent in the binary solvent mixture

$$- (V_A/V_C)\phi_C^\circ[\phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)]/[1 + \phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C)]$$

and in the pure alcohol itself

$$+ (V_A K_C \phi_C^\circ/V_C^2)(1 + K_C/V_C)^{-1}$$

Similar changes will now be made to eq 4.28. Both the numerator and denominator of terms describing alcohol B's and C's hydrogen-bonding in the ternary system will be extended by adding $\phi_D^\circ(K_{B(\text{or } C)D}/V_D)$. The terms describing the hydrogen-bonding effects of the third alcohol cosolvent in the ternary mixture are

$$- (V_A/V_D)\phi_D^\circ[\phi_B^\circ(K_{DB}/V_B) + \phi_C^\circ(K_{DC}/V_C) + \phi_D^\circ(K_D/V_D)]/$$

$$[1 + \phi_B^\circ(K_{DB}/V_B) + \phi_C^\circ(K_{DC}/V_C) + \phi_D^\circ(K_D/V_D)]$$

and in pure alcohol D itself

$$+ (V_A K_D \phi_D^\circ/V_D^2)(1 + K_D/V_D)^{-1}$$

Making the afore-mentioned changes to eq 4.28, the following ezpression

$$\ln \phi_A^{sat} = \phi_B^\circ \ln(\phi_A^{sat})_B + \phi_C^\circ \ln(\phi_A^{sat})_C + \phi_D^\circ \ln(\phi_A^{sat})_D -$$

$$0.5[\ln(\chi_B^\circ V_B + \chi_C^\circ V_C + \chi_D^\circ V_D) - \phi_B^\circ \ln V_B - \phi_C^\circ \ln V_C - \phi_D^\circ \ln V_D] -$$

$$(V_A/V_B)\phi_B^\circ[\phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C) + \phi_D^\circ(K_{BD}/V_D)]/$$

$$[1 + \phi_B^\circ(K_B/V_B) + \phi_C^\circ(K_{BC}/V_C) + \phi_D^\circ(K_{BD}/V_D)] +$$

$$(V_A K_B \phi_B^\circ/V_B^2)(1 + K_B/V_B)^{-1} - (V_A/V_C)\phi_C^\circ[\phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C) + \phi_D^\circ(K_{CD}/V_D)] /$$

$$[1 + \phi_B^\circ(K_{CB}/V_B) + \phi_C^\circ(K_C/V_C) + \phi_D^\circ(K_{CD}/V_D)] + (V_A K_C \phi_C^\circ/V_C^2)(1 + K_C/V_C)^{-1} +$$

$$(V_A/V_D)\phi_D^\circ[\phi_B^\circ(K_{DB}/V_B) + \phi_C^\circ(K_{DC}/V_C) + \phi_D^\circ(K_D/V_D)]/$$

$$[1 + \phi_B^\circ(K_{DB}/V_B) + \phi_C^\circ(K_{DC}/V_C) + \phi_D^\circ(K_D/V_D)] + (\phi_D^\circ K_D V_A/V_D^2)/[1 + (K_D/V_D)] +$$

$$[\phi_B^\circ\phi_C^\circ(\delta_B' - \delta_C')^2 + \phi_B^\circ\phi_D^\circ(\delta_B' - \delta_D')^2 + \phi_C^\circ\phi_D^\circ(\delta_C' - \delta_D')^2]V_A(RT)^{-1}$$

Equation 4.32

is obtained for predicting the solubility of a sparingly soluble solute ($\phi_A^{sat} \approx 1$) in a ternary alcohol + alcohol + alcohol solvent mixture.

There is a very limited amount of solubility data in the published chemical literature for solutes dissolved in ternary solvent mixtures containing only alcohol cosolvents. All of the published data pertains to 2-butoxyethanol with a propanol and butanol isomer. As noted in an earlier section, McHale et al.[78] showed that an

alkoxyalcohol can be treated as a monofunctional alcohol in the Mobile Order theory solubility predictions. The summarized computations given in Tables VI and VII further support this observation. The last column of Table VIII compares the experimental anthracene solubility data in four ternary 2-butoxyethanol + propanol + butanol solvent mixtures to predicted values based upon eq 4.32. All homogeneous self-association (K_B, K_C, and K_D) and heterogeneous cross-association (K_{BC}, K_{CB}, K_{BD}, K_{DB}, K_{DB} and K_{DC}) were set equal to 5,000 cm^3 mol^{-1}. Numerical entries in Table VIII reveal that eq 4.32 predicts the observed solubility data to within ± 3.6%, which is only slightly more than twice the experimental uncertainty associated with each measured anthracene mole fraction solubility. Based upon my computations, I conclude that there is no loss in predictive accuracy in extending Mobile Order theory to ternary solvent systems that contain three alcohol and/or alkoxyalcohol cosolvents.

Extension of Kretschmer–Wiebe Association Model to Ternary Alcohol + Alkane + Alkane Solvent Systems

The Kretschmer–Wiebe association model, discussed in Chapter II, is one of the more popular solution models used by chemical engineers to describe the thermodynamic properties of nonelectrolyte solutions containing alcohol molecules. Unlike Mobile Order theory, the Kretschmer–Wiebe association model assumes discrete association complexes. Acree and Tucker[70] previously showed that expressions derived from the Kretschmer–Wiebe association model predicted the solubility behavior of anthracene in thirty binary alkane + alcohol solvent systems to within ± 8%, using numerical values for

the alcohol association constants calculated from vapor-liquid equilibria and calorimetric excess enthalpy data. To date, the Kretschmer–Wiebe association model has not been used to predict solubilities in ternary alcohol + alkane + alkane solvent mixtures.

Extension of the Kretschmer–Wiebe association model to systems of an inert crystalline solute (component A) dissolved in ternary alcohol (B) + alkane (C) + alkane (D) solvent systems is relatively straightforward. The derivation is similar to that given in Chapter 2, except that the chemical contribution

$$(\Delta G_{ABCD})_{chem} = RT[n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln \phi_C + n_D \ln \phi_D + \chi_B K_B(\hat{\phi}_{B1} - \hat{\phi}_{B1}^{*})]$$

Equation 4.33

contains one additional logarithm term for the second alkane cosolvent, while the physical contribution

$$(\Delta G_{ABCD})_{phys} = (n_A V_A + \Sigma\, n_{Bi} V_B + n_C V_C + n_D V_D)^{-1} \times$$

$$[\Sigma\, n_A V_A n_{Bi} V_{Bi}(\delta_A' - \delta_{Bi}')^2 + n_A V_A n_C V_C(\delta_A' - \delta_C')^2 + n_A V_A n_D V_D(\delta_A' - \delta_D')^2 +$$

$$\Sigma\, n_{Bi} V_{Bi} n_C V_C(\delta_{Bi}' - \delta_C')^2 + \Sigma\, n_{Bi} V_{Bi} n_D V_D(\delta_{Bi}' - \delta_D')^2 + n_C V_C n_D V_D(\delta_C' - \delta_D')^2]$$

Equation 4.34

contains several additional terms describing all pair-wise molecular interactions involving the second alkane cosolvent. The final derived expression for the solubility of the crystalline solute is

$$\ln \phi_A^{sat} = \phi_B^{\circ} \ln(\phi_A^{sat})_B + \phi_C^{\circ} \ln(\phi_A^{sat})_C + \phi_D^{\circ} \ln(\phi_A^{sat})_D - \phi_B^{\circ}(V_A/V_B)K_B(\hat{\phi}_{B1} - \hat{\phi}_{B1}^{*}) +$$

$$V_A(RT)^{-1}[\phi_B^{\circ}\phi_C^{\circ}(\delta_B' - \delta_C')^2 + \phi_B^{\circ}\phi_D^{\circ}(\delta_B' - \delta_D')^2 + \phi_C^{\circ}\phi_D^{\circ}(\delta_C' - \delta_D')^2]$$

Equation 4.35

obtained by differentiating the excess Gibbs energy, G_{ABCD}^{E}

$$G_{ABCD}^{E} = (\Delta G_{ABCD})_{chem} + (\Delta G_{ABCD})_{phys} \qquad \text{Equation 4.36}$$

with respect to the number of moles of solute. As in earlier derivations, the terms involving the modified solubility parameters of the crystalline solute have been mathematically eliminated from the final derived equation using the measured solute solubilities in the pure solvents. The concentrations of the alcohol monomer, $\hat{\phi}_{B1}$ and $\hat{\phi}_{B1}^{*}$, are calculated using

$$\hat{\phi}_{B_1} = [2K_B\phi_B^{\circ} + 1 - (1 + 4K_B\phi_B^{\circ})^{1/2}]/2K_B^{2}\phi_B^{\circ} \qquad \text{Equation 4.37}$$

and

$$\hat{\phi}_{B_1}^{*} = [2K_B + 1 - (1 + 4K_B)^{1/2}]/2K_B^{2} \qquad \text{Equation 4.38}$$

known values of the Kretschmer–Wiebe association constants: K_B = 197 (1-propanol); K_B = 131 (2-propanol); K_B = 175 (1-butanol); and K_B = 68 (2-butanol).[100-104] Careful examination of eq 4.34 and eq 2.85 that irrespective of whether the solvent mixture contains one or two alkane cosolvents, the concentration of the alcohol monomer, $\hat{\phi}_{B_1}$, is still calculated the same. The calculation depends only upon the K_B and the stoichiometric volume fraction composition of the alcohol in the mixed solvent, and not upon either the physical properties or number of alkane cosolvents. Like Mobile Order theory, the Kretschmer–Wiebe association model is easily extended to solvent mixtures containing any number of alkane cosolvents.

The predictive ability of the Kretschmer–Wiebe association model is given in the last column of Table V for anthracene dissolved in eight ternary alcohol + alkane + alkane solvent mixtures. The Kretschmer–Wiebe association model predicts the

observed solubility behavior in this eight solvent mixtures to within an overall average deviation ± 8.21%, which is comparable to the deviations found in using eq 4.28 of Mobile Order theory. No statistical significance is placed upon the apparent small superiority of eq 4.28 as the experimental uncertainties of ± 1.5% far exceeds the small ± 0.3% difference in predictive accuracy. Equation 4.28 and eq 4.35 (Kretschmer–Wiebe association model equation) both treat anthracene as an inert solute incapable of complexation with surrounding solvent molecules; hence, the comparison in Table V should represent an unbiased test of the limitations of Mobile Order theory versus the Kretschmer–Wiebe association model. Both solution models are viewed as equivalent as far as the eight anthracene systems are concerned. This is important in that the Kretschmer–Wiebe association model is considered to be the more conventional thermodynamic model of the two. The Kretschmer–Wiebe association model assumes discrete association complexes, which is in line with more traditional thermodynamic approaches. Mobile Order theory, on the other hand, treats solutions in terms of the fraction of time that a molecule is "free" or "bound" to an adjacent molecule. To thermodynamicists, theoretical treatments that invoke "time fractions" are more nebulous than the more conventional treatments that involve specific, well-defined molecular complexes. It is hoped that once the benefits of Mobile Order theory are fully recognized, both in terms of its mathematical simplicity and comparable (and often superior) predictive ability, that researchers will begin using Mobile Order to a greater extent.

The predictive accuracy of Mobile Order theory and the Kretschmer–Wiebe association model are roughly the same whenever anthracene is treated as inert solute. This is not the case, however, when one extends the basic model to include solute-solvent complexation. As shown in the second numerical column of Table V inclusion of solute-solvent complexation significantly improves the predictive accuracy of Mobile Order theory. The average absolute deviation drops from approximately ± 7.94% (eq 4.28) to ± 3.99%. The Kretschmer–Wiebe association model is not easily extended to such complexing systems. One would have to deal with solute complexation with the alcohol monomers

$$A + B_1 \rightleftharpoons B_1 \qquad K_{AB1} = \hat{\phi}_{AB1}/\hat{\phi}_A\hat{\phi}_{B1}$$

as well as all of the different alcohol self-associated species

$$A + B_i \rightleftharpoons B_i \qquad K_{ABi} = \hat{\phi}_{ABi}/\hat{\phi}_A\hat{\phi}_{Bi}$$

There would be an equilibrium constant for each solute-alcohol complex presumed. Even if simplifying assumptions could be found to reduce the number of equilibrium constants to a reasonable number, one would still be faced with having to calculate $\hat{\phi}_{B1}$ through a series of re-iterative computations. Computational simplicity is one of the major advantages that Mobile Order theory has over the more conventional thermodynamic solution models like the Kretschmer–Wiebe association model.

Extension of Mecke–Kempter Association Model for Ternary Solvent Systems

The Mecke–Kempter association model, discussed in Chapter II, is also a popular model used by chemical engineers to describe the thermodynamic properties of nonelectrolyte solutions containing alcohol molecules. Like the Kretschmer–Wiebe association model, the Mecke–Kempter association model assumes discrete association complexes. Acree et al.[69] previously showed that expressions derived from the Mecke–Kempter association model predicted the solubility behavior of anthracene in thirty binary alkane + alcohol solvent systems to within ± 9.4%, using numerical values from vapor-liquid equilibria and calorimetric excess enthalpy data. To date, the Mecke–Kempter association model has not been used to predict solubilities in ternary alcohol + alkane + alkane solvent mixtures.

Extension of the Mecke–Kempter association model to systems of an inert crystalline solute (component A) in ternary alcohol (B) + alkane (C) + alkane (D) solvent systems is relatively straightforward. The derivation is identical to the derivation for the Kretschmer–Wiebe association model. The physical contribution is the same as the physical contribution (eq 4.31) for the Kretschmer–Wiebe association model. The chemical contribution, as in the case of the Kretschmer–Wiebe association model, contains one additional logarithm term for the second alkane cosolvent. The final derived expression for the solubility of a crystalline solute is

$$\ln \phi_A^{sat} = \phi_B^\circ \ln(\phi_A^{sat})_B + \phi_C^\circ \ln(\phi_A^{sat})_C + \phi_D^\circ \ln(\phi_A^{sat})_D + (V_A/K_B V_B) \times$$

$$[\ln(1 + K_B\phi_B^\circ) - \phi_B^\circ \ln(1 + K_B)] +$$

$$V_A[\phi_B^\circ \phi_C^\circ(\delta_B' - \delta_C')^2 + \phi_B^\circ \phi_D^\circ(\delta_B' - \delta_D')^2 + \phi_C^\circ \phi_D^\circ(\delta_C' - \delta_D')^2](RT)^{-1}$$

Equation 4.39

obtained by differentiating the excess Gibbs energy (eq 4.36) with respect to the number of moles of solute. As in other derivations, the terms involving the modified solubility parameters of the crystalline solute have been mathematically eliminated from the final derived equation using the measured solute solubilities in the pure solvents. The concentrations of the alcohol monomer are calculated, as for the Kretschmer–Wiebe association model, eqs 4.37 and 4.38 using known values of the Mecke–Kempter constants: $K_B = 240$ (1-propanol); $K_B = 186$ (2-propanol); $K_B = 208$ (1-butanol); and $K_B = 90$ (2-butanol). Once again, the concentration of the alcohol monomer, $\hat{\phi}_{B1}$, is calculated the same whether the solvent mixture contains one or two alkane cosolvents. The calculation depends only upon K_B and the stoichiometric volume fraction composition of the alcohol in the mixed solvent, and not upon either the physical properties or number of alkane cosolvents. Like the Kretschmer–Wiebe association model and Mobile Order theory, the Mecke–Kempter association model is easily extended to solvent mixtures containing any number of alkane cosolvents.

The predictive ability of the Mecke–Kempter association model is given in the third numerical column of Table V for anthracene dissolved in eight ternary alcohol + alkane + alkane solvent mixtures. The Mecke–Kempter association model predicts the observed solubility behavior in these eight solvent mixtures to within an overall average

deviation of ± 8.77% which is comparable to the deviations found in using eq 4.28 of Mobile Order theory. No statistical significance is placed upon the apparent small superiority of eq 4.28 as the experimental uncertainties of ± 1.5% far exceeds the small ± 0.8% difference in predictive accuracy. Equation 4.28 (Mobile Order) and eq 4.39 (Mecke–Kempter) both treat anthracene as an inert solute incapable of complexation with surrounding solvent molecules; hence, the comparison in Table V should represent an unbiased test of the limitations of Mobile Order theory versus the Mecke–Kempter association model. Both solution models are viewed as equivalent as far as the eight anthracene systems are concerned. This is important in that the Mecke–Kempter association model is considered to be the more conventional thermodynamic model of the two. The Mecke–Kempter association model assumes discrete association complexes, which is in line with more traditional thermodynamic approaches. Mobile Order theory, on the other hand, treats solutions in terms of fractions of time that a molecule is "free" or "bound" to an adjacent molecule. To thermodynamicists, theoretical treatments that invoke "time fractions" are more nebulous than the more conventional treatments that involve specific, well-defined molecular complexes. It is hoped that once the benefits of Mobile Order theory are recognized, both in terms of its mathematical simplicity and comparable (and often superior) predictive ability, that researchers will begin using Mobile Order theory to a greater extent.

The predictive accuracy of Mobile Order theory and the Mecke–Kempter association model are roughly the same whenever anthracene is treated as an inert solute. This is not the case, however, when one extends the basic model to include solute-solvent

complexation. As shown in the second numerical column of Table V, inclusion of solute-solvent complexation significantly improves the predictive accuracy of Mobile Order theory. As previously mentioned, the average absolute deviation drops from ± 7.94% (eq 4.28) to ± 3.99% (eq 4.29). The Mecke–Kempter association model is not easily extended to such complexing systems for the same reasons the Kretschmer–Wiebe association model cannot be easily extended to such systems. One would have to deal with solute complexation with the alcohol monomer as well as all of the different alcohol self-associated species. There would be an equilibrium constant for each solute-alcohol complex presumed. Even if simplifying assumptions could be found to reduce the number of equilibrium constants to a reasonable number, one would still be faced with having to calculate $\hat{\phi}_{B1}$ through a series of re-iterative computations. Computational simplicity is one of the major advantages of Mobile Order theory over the more conventional thermodynamic solution models like the Mecke–Kempter association model.

Conclusions

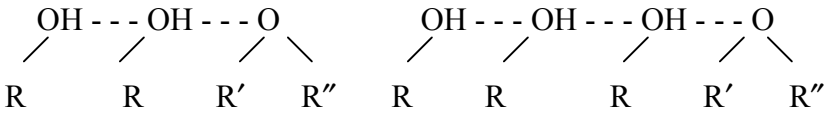
For most systems that are available for analysis in the published literature, extending the predictive equation of the Mobile Order theory, Mecke–Kempter, or Kretschmer–Wiebe association models from binary solvent systems to ternary solvent systems gave little or no loss of accuracy in predicting the solubility of a sparingly soluble solute. There is very little difference between the predictive abilities of these models. This is an interesting observation, since Mobile Order theory is concerned only with the fraction of time that a molecule participates in hydrogen bonding and not with

the concentration of any particular species in solution, as are the Mecke–Kempter and Kretschmer–Wiebe association models.

In the case of the 2-alkoxyalcohol + alcohol + alcohol systems we studied, Mobile Order theory retained its predictive ability for the four systems in the published data. I could not compare Mobile Order theory predictions for these systems with the predictions of the Mecke–Kempter and Kretschmer–Wiebe association models because we cannot solve those two models without lengthy reiterative calculations. Those types of calculations cannot be performed in Microsoft Excel where all the other calculations were performed. That fact alone makes Mobile Order theory an easier model to use to predict the solubility of a sparingly soluble solute in many systems.

Future Investigations

It would seem reasonable that the next step would be to look at ternary systems consisting of an ether + alcohol + alkane. The alcohol will self-associate. The ether, however, will not self-associate. Moreover, each time an ether molecule forms a hydrogen bond with an alcohol, the chain is broken.



I would guess that shorter chains would allow anthracene to dissolve more readily as the anthracene would be able to fit more easily between the chains. The solubility data for anthracene dissolved in ternary dibutyl ether + alcohol + alkane, etc. solvent mixtures

which was measured as part of this dissertation research, will be invaluable in assessing the limitations and applications of any future Mobile Order theory equations derived for such ternary solvent systems.

Another possible research area would be that of investigating the solubility of PAHs in diols. Smaller diols tend to be rather viscous and are not always miscible with alcohol cosolvents. This might present a problem in terms of getting equilibrated mixtures. However, longer chain diols such as 1,5-pentane-diol or 1,6-hexane-diol might give the necessary equilibrated mixtures. I would expect a lower solubility due to the increased possibility for hydrogen bonding with two functional OH groups on each diol.

So far, we have looked at about twenty-fold solubility differences. We could look at compounds that would give a much greater solubility differences. The systems studied to date have involved molecules with molar volumes fairly close in size. It would be possible to use solvent molecules that vary greatly in size. An example is hexadecanol mixed with propanol. No one has experimented yet with a functional group on the PAH itself. Possibly, someone could look at multicomponent solvent systems (larger that the ternary systems I studied) with each of these new variations.

There are still many factors concerning polycyclic aromatic hydrocarbons to be studied before solubilities are fully understood and completely predictable. Although computers help make the calculations faster, they will not take the place of scientists going into the lab to make experimental determinations. It will be some time yet before the mystery is finally unraveled.

Table II

Summarized Comparison Between Experimental Solubilities of Anthracene in Ternary Solvent Mixtures and Predicted Values Based Upon Mobile Order Theory

1-PrOH + 1-BtOH + cyclohexane	4.4	2.6
1-PrOH + 2-BtOH + cyclohexane	7.7	3.3
2-PrOH + 1-BtOH + cyclohexane	7.0	1.6
2-PrOH + 2-BtOH + cyclohexane	10.1	3.9
1-PrOH + 1-BtOH + heptane	1.6	6.3
1-PrOH + 2-BtOH + heptane	3.3	4.5
2-PrOH + 1-BtOH + heptane	3.7	3.9
2-PrOH + 2-BtOH + heptane	6.1	1.8
1-PrOH + 1-BtOH + 2,2,4-trimethylpentane	2.0	9.5
1-PrOH + 2-BtOH + 2,2,4-trimethylpentane	2.3	7.1
2-PrOH + 1-BtOH + 2,2,4-trimethylpentane	1.1	7.8
2-PrOH + 2-BtOH + 2,2,4-trimethylpentane	2.4	5.1

Table II (continued)

Ternary Solvent System[a]				
Alcohol	Alkane	Alkane	Deviations (%)[b]	
(B)	(C)	(D)	Eq 4.28	Eq 4.29
1-PrOH	2,2,4-trimethylpentane	cyclohexane	6.9	4.1
2-PrOH	2,2,4-trimethylpentane	cyclohexane	7.5	3.4
1-BtOH	2,2,4-trimethylpentane	cyclohexane	4.9	3.2
2-BtOH	2,2,4-trimethylpentane	cyclohexane	11.4	5.2
1-PrOH	heptane	cyclohexane	5.2	4.3
2-PrOH	heptane	cyclohexane	10.1	2.5
1-BtOH	heptane	cyclohexane	5.0	2.9
2-BtOH	heptane	cyclohexane	12.5	6.5
		Overall Average Deviation	5.8	4.5

[a] Abbreviation of solvents: 1-propanol (1-PrOH); 2-propanol (2-PrOH); 1-butanol (1-BtOH); and 2-butanol (2-BtOH).

[b] Deviation (%) = $(100/N)\ \Sigma\ |\ [(\chi_A^{sat})^{calc} - (\chi_A^{sat})^{exp}]/(\chi_A^{sat})^{exp}\ |$, where N corresponds to the number of data points for each ternary system. In the present study, solubilities were detemined at 19 different ternary solvent compositions.

Table III

Solvent and Solute Properties Used in Mobile Order Predictions

Component (*i*)	V_i /(cm^3 mol^{-1})	δ_i' /($MPa^{1/2}$)[a]
n-Heptane	147.48	14.66
Cyclohexane	108.76	14.82
2,2,4-Trimethylpentane	166.09	14.30
1-Propanol	75.10	17.29
2-Propanol	76.90	17.60
1-Butanol	92.00	17.16
2-Butanol	92.4	16.60
2-Methoxyethanol	79.40	20.80
2-Ethoxyethanol	97.50	20.30
2-Propoxyethanol	114.92	19.80
2-Butoyxethanol	131.92	19.20
Anthracene	150.0	$a_A^{solid} = 0.01049$[b]

[a] Tabulated values are taken from a compilation given in Ruelle et al.[47,49,51,54] or are estimated using known values for similar alcohols. Modified solubility parameters for the four 2-alkoxyalcohols were estimated by McHale et al.[47,49,51,54,78]

[b]The numerical value of $a_A^{solid} = 0.01049$[105] was calculated from the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature of the solute, $T_{mp} = 515K$.

Table IV

Per Cent Deviation in Predicted Anthracene Solubilities Compared to Measured

Anthracene Solubilites in Ternary Solvent Systems as KAB Varies

Solvent B=	2-propanol	2-propanol	2-butanol
Solvent C=	heptane	2,2,4-trimethylpentane	heptane
Solvent D=	cyclohexane	cyclohexane	cyclohexane

KAB	Average Deviation	Average Deviation	Average Deviation
75	6.131	4.253	9.701
80			
90			
95		3.418	
100	4.037	3.351	8.151
105		**3.310**	7.825
110		**3.310**	7.495
115		3.322	7.160
120	2.697	3.332	6.822
125	2.475	3.374	6.480
130	2.252		
135	2.054		
140	1.882		
145	**1.825**		
150	1.874	4.203	4.731
155	2.006		
175	3.066	5.951	3.039
200	5.201	8.304	1.924
205			1.808
210			1.692
215			**1.605**
220			1.621
225		10.751	1.714
230			1.828
250		13.199	2.846
275		15.642	
300	14.708	18.075	6.354
500	33.174	37.025	21.104

Table IV (continued)

Solvent B=	2-butanol	1-propanol	1-propanol
Solvent C=	2,2,4-trimethylpentane	heptane	2,2,4-trimethylpentane
Solvent D=	cyclohexane	cyclohexane	cyclohexane

KAB	Average Deviation	Average Deviation	Average Deviation
50		3.535	
70		2.822	
75	8.501	2.688	3.719
80		**2.585**	
85		2.620	
90	7.560	2.702	3.281
95	7.234	2.837	**3.252**
100	6.902	3.003	3.263
105	6.565	3.184	3.310
110	6.224	3.415	3.456
115	5.879	3.669	3.655
120	5.530	3.958	3.853
125	5.177	4.261	4.052
130			
140			
150	3.574	6.366	5.297
155			
175	2.416	8.858	7.028
195	1.834		
200	**1.783**	11.418	9.411
205	1.810		
210			
220			
225	2.450		
230			
250	4.204	16.553	14.457
300		21.664	19.478
500	23.241	41.493	38.966

Table IV (continued)

Solvent B=	1-butanol	1-butanol
Solvent C=	heptane	2,2,4-trimethylpentane
Solvent D=	cyclohexane	cyclohexane

KAB	Average Deviation	Average Deviation
50		
70		
75	2.779	3.013
80		
90	2.569	
95	**2.534**	2.668
100	2.559	**2.611**
105	2.593	2.662
110	2.631	2.751
115	2.688	2.880
120	2.753	3.042
125	2.883	3.206
130		3.395
140		
150	4.097	4.348
175	5.852	6.115
200	7.865	8.103
210		
220		
225		10.188
230		
250	12.021	12.283
275		14.382
300	16.196	16.481
500	32.613	32.996

Table V

Average Deviation for the Predicted Solubility of Anthracene in Ternary Solvent Systems

System	Cosolvents	Mobile Order Theory eq 4.28	Mobile Order Theory eq 4.29	Mecke-Kempter Theory	Kretschmer-Wiebe Theory
1.	1-butanol 2,2,4-trimethylpentane cyclohexane	4.86	3.21	5.97	5.42
2.	1-butanol heptane cyclohexane	4.99	2.88	5.72	5.17
3.	2-butanol heptane cyclohexane	12.52	6.48	12.03	11.72
4.	2-butanol 2,2,4-trimethylpentane cyclohexane	11.42	5.18	11.3	11.31
5.	1-propanol heptane cyclohexane	5.25	4.26	6.54	5.81
6.	1-propanol 2,2,4-trimethylpentane cyclohexane	6.94	4.05	8.74	8.03
7.	2-propanol heptane cyclohexane	10.11	2.48	10.96	10.16
8.	2-propanol 2,2,4-trimethylpentane cyclohexane	7.48	3.37	8.86	8.04
Overall Average Deviation=		7.94	3.99	8.77	8.21

Table VI

Average Deviation for the Predicted Solubility of Anthracene in Ternary Solvent Systems Consisting of an Alkoxyalcohol, + Alkane + Alkane

System	Cosolvents	Mobile Order Theory eq 4.28	Mobile Order Theory eq 4.29
1.	2-butoxyethanol heptane cyclohexane	5.04	7.58
2.	2-butoxyethanol 2,2,4-trimethylpentane cyclohexane	7.07	3.34
3.	2-ethoxyethanol heptane cyclohexane	5.75	10.08
4.	2-ethoxyethanol 2,2,4-trimethylpentane cyclohexane	5.51	9.13
Overall Average Absolute Deviation=		5.84	7.53

Table VII

Average Deviation for the Predicted Solubility of Anthracene in Ternary Solvent Systems Consisting of an Alkoxyalcohol + Alcohol + Alkane

System		Mobile Order Theory eq 4.28	Mobile Order Theory eq 4.29
1.	2-butoxyethanol 1-propanol heptane	2.85	6.44
2.	2-butoxyethanol 1-propanol cyclohexane	3.72	4.92
3.	2-butoxyethanol 2-propanol heptane	4.83	4.97
4	2-butoxyethanol 2-propanol cyclohexane	7.07	3.34
	Overall Average Absolute Deviation=	4.62	4.92

Table VIII
Average Absolute Deviation for the Predicted Solubility of Anthracene in Ternary Solvent Systems Consisting of an Alkoxyalcohol + Alcohol + Alcohol

System	Cosolvents	Mobile Order Theory eq 4.32
1	2-butoxyethanol 1-propanol 1-butanol	1.7
2	2-butoxyethanol 1-propanol 2-butanol	2.4
3	2-butoxyethanol 2-propanol 1-butanol	5.1
4	2-butoxyethanol 2-propanol 2-butanol	5.1
	Overall absolute average deviation=	3.6

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APPENDIX I

GLOSSARY OF SYMBOLS

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
A	measured absorbance in the Beer–Lambert law
A_{ij}	NIBS binary interaction parameter independent of composition
b	path length in the Beer–Lambert law
BCF	bioconcentration factor which is defined as the equilibrium ratio of the concentration of the substance in the exposed organism to the concentration of the dissolved substance in the surrounding environment
c	concentration (mol L^{-1}) of the solution in the Beer–Lambert law
c_i	cohesive energy density for Scatchard–Hildebrand theory, defined by $\Delta U_i^{vap}/V_i$
C_i	molar concentration of component *i*
$\hat{C}_{Ai}$	molar concentration of the *i*-mer in the Kretschmer–Wiebe association model
ΔC_P	difference between heat capacities of the solid and subcooled liquid solute, used in the computation of a_A^{solid}
ΔG^E	excess Gibbs energy (J mol^{-1})

ΔG_A^{fh}	partial molar Gibbs energy of the solute (Flory–Huggins model), extrapolated back to infinite dilution
ΔG_{ABCD}^{mix}	Gibbs energy of mixing for the ternary system
ΔH_A^{fus}	molar enthalpy of fusion of the solid solute at its normal melting point temperature
ΔH_{ABC}^{E}	excess molar enthalpy of mixing of the ternary non-electrolyte solution
i g	ideal gas
K_{BC}, K_{CB}	Mobile Order cross-association stability (equilibrium) constant describing the heterogeneous association of monofunctional alcohols B and C, where the concentration units are molarity
K_C	association constant for Mobile Order model ($cm^3\ mol^{-1}$)
K_C^*	association constant for Kretschmer–Wiebe model
liq	liquid
n_i	number of moles of component *i*
p_a	Raoult's law partial pressure of species A in the vapor
p_a°	Raoult's law pressure of the vapor above the pure component
PAHs	polycyclic aromatic hydrocarbons
Q	functions expressing the differences between predicted and observed values
R	universal gas constant ($J\ mol^{-1}\ K^{-1}$)
S_i	curve-fit coefficient for the Combined NIMS/Redlich–Kister model which is derived from sub-binary solvent mixtures via a least squares analysis

SOC semivolatile organic compound

ΔS^{mix} entropy of mixing in the Mobile Order model

T temperature (K)

tm ternary mixture

T_{mp} normal melting point temperature of the solute (K)

ΔU_i^{vap} energy required for the isothermal vaporization of the saturated liquid to the ideal gas state

V_i molar volume of component *i*

X Flory interaction parameter

Z any extensive thermodynamic property

Greek letter

β_{AB}, β_{AC} solute-solvent interaction parameters in the Kretschmer–Wiebe association model

χ_B° mole fraction compositions of the binary or ternary solvent mixture, calculated as if the solute were not present

χ_A^{sat} mole fraction solubility of the solute

Γ_i generalized weighting factor for component *i*, used in the Nearly Ideal Binary Solvent (NIBS) model for nonspecific interactions

γ_A liquid phase activity coefficient of component A

γ_{BH} fraction of time that alcohol solvent B is not involved in hydrogen-bond formation

δ	solubility parameter, the positive square root of c
δ_i'	modified solubility parameter of component *i*
ε	molar absorptivity (cm^{-1} mol^{-1} L)
ϕ_A^{sat}	ideal volume fraction solubility of the solute
ϕ_B^0	ideal volume fraction composition of the binary or ternary solvent mixture, calculated as if the solute was not present
μ_i	chemical potential of component *i*
τ_{AB}	$\exp[-(u_{AB} - u_{BB})/RT]$
Ψ_{Total}	total molar concentration of all true species in associated solution
$\Psi_B^*, \Psi_C^*, \Psi_D^*$	total molar concentration of all species in the neat alcohol cosolvents

Subscripts

phys	contribution to G^E from physical interactions
chem	contribution to G^E from chemical interactions
conf	contribution to G^E from configurational interactions

Superscripts

sat	indicates a saturated solution
º	indicates that solvent composition is calculated as if the solute were not present
^	true species that exist in the associated solution

Appendix II – DATA TABLES

Table IX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Butanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3714	0.3413	0.004202
0.1720	0.6948	0.001972
0.2908	0.2681	0.004046
0.2791	0.5032	0.003094
0.7231	0.1074	0.007562
0.7159	0.1952	0.006997
0.2179	0.6892	0.002197
0.1276	0.5197	0.002149
0.4196	0.4873	0.003898
0.5203	0.3880	0.004816
0.1852	0.1713	0.003235
0.7253	0.1460	0.007327
0.5313	0.2525	0.005721
0.1316	0.2234	0.002654
0.1199	0.7040	0.001725
0.2390	0.1234	0.003779
0.1300	0.4238	0.002362
0.4455	0.1127	0.005672
0.5417	0.1124	0.006553

Table X

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3419	0.3906	0.003921
0.1437	0.7402	0.001604
0.2742	0.3107	0.003625
0.2542	0.5457	0.002793
0.7091	0.1240	0.007311
0.6853	0.2293	0.006388
0.1887	0.7314	0.001845
0.1125	0.5739	0.001866
0.3795	0.5369	0.003456
0.4784	0.4381	0.004384
0.1771	0.2058	0.003079
0.6976	0.1803	0.006711
0.5025	0.2936	0.005290
0.1199	0.2684	0.002502
0.1043	0.7444	0.001443
0.2339	0.1445	0.003702
0.1165	0.4773	0.002106
0.4377	0.1362	0.005574
0.5291	0.1354	0.006337

Table XI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3712	0.4165	0.003703
0.1536	0.7590	0.001606
0.3074	0.3502	0.003491
0.2641	0.5860	0.002585
0.7397	0.1349	0.007021
0.6998	0.2406	0.006017
0.1930	0.7471	0.001822
0.1225	0.6222	0.001786
0.3907	0.5470	0.003299
0.4856	0.4491	0.004110
0.2154	0.2433	0.002909
0.7117	0.1964	0.006375
0.5300	0.3409	0.004906
0.1528	0.3148	0.002429
0.1116	0.7763	0.001409
0.2817	0.1617	0.003554
0.1363	0.5273	0.002020
0.4946	0.1541	0.005229
0.5777	0.1538	0.005803

TableXII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Butanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3227	0.4227	0.003575
0.1682	0.7013	0.001818
0.2937	0.2668	0.003890
0.2778	0.5023	0.003098
0.7240	0.1099	0.007256
0.7141	0.1970	0.006709
0.2203	0.6864	0.002124
0.1254	0.5180	0.002080
0.4220	0.4836	0.003779
0.5181	0.3865	0.004627
0.1827	0.1763	0.003137
0.7201	0.1510	0.007111
0.5324	0.2521	0.005721
0.1334	0.2259	0.002723
0.1197	0.7054	0.001600
0.2401	0.1226	0.003790
0.1281	0.4236	0.002310
0.4492	0.1133	0.005575
0.5420	0.1115	0.006332

Table XIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Methyl-1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3721	0.3373	0.003942
0.1727	0.6946	0.001615
0.2899	0.2726	0.003642
0.2805	0.5009	0.002688
0.7276	0.1055	0.007223
0.7153	0.1935	0.006340
0.2321	0.6752	0.001885
0.1277	0.5149	0.001858
0.4243	0.4828	0.003416
0.5263	0.3845	0.004381
0.1906	0.1188	0.003291
0.6442	0.1900	0.006236
0.5355	0.2505	0.005275
0.1403	0.2208	0.002622
0.1224	0.7002	0.001382
0.2507	0.1208	0.003816
0.1281	0.4287	0.002072
0.4406	0.1124	0.005454
0.5388	0.1185	0.006045

Table XIV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3454	0.3819	0.003745
0.1522	0.7289	0.001449
0.2732	0.3062	0.003510
0.2472	0.5579	0.002514
0.7089	0.1240	0.007040
0.6887	0.2255	0.006059
0.1907	0.7289	0.001636
0.1124	0.5677	0.001771
0.3806	0.5317	0.003211
0.4838	0.4300	0.003943
0.1840	0.1975	0.003121
0.7017	0.1760	0.006600
0.5041	0.2918	0.005073
0.1245	0.2594	0.002507
0.1045	0.7401	0.001248
0.2388	0.1420	0.003656
0.1177	0.4675	0.002004
0.4414	0.1324	0.005403
0.5309	0.1327	0.006263

Table XV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3675	0.4154	0.003551
0.1522	0.7588	0.001408
0.3065	0.3374	0.003358
0.2740	0.5728	0.002476
0.7351	0.1327	0.006720
0.7021	0.2307	0.005916
0.2017	0.7363	0.001642
0.1216	0.6242	.oo1593
0.3939	0.5433	0.003137
0.4911	0.4421	0.004024
0.2134	0.2442	0.002804
0.7214	0.1835	0.006332
0.5299	0.3067	0.004814
0.1573	0.3073	0.002344
0.1135	0.7663	0.001225
0.2785	0.1774	0.003318
0.1279	0.5364	0.001798
0.4940	0.1587	0.004969
0.5810	0.1525	0.005899

Table XVI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.4126	0.3784	0.003645
0.1800	0.7311	0.001842
0.3476	0.3129	0.003398
0.3025	0.5422	0.002818
0.7721	0.1123	0.006796
0.7336	0.2039	0.006256
0.2219	0.7118	0.002104
0.1431	0.5956	0.001775
0.4396	0.4986	0.003752
0.5378	0.3996	0.004567
0.2378	0.2256	0.002389
0.7535	0.1575	0.006357
0.5751	0.2735	0.005086
0.1659	0.2925	0.002014
0.1281	0.7505	0.001547
0.3010	0.1574	0.002888
0.1510	0.5004	0.001891
0.5303	0.1386	0.004769
0.6200	0.1263	0.005643

Table XVII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3978	0.3721	0.004077
0.1791	0.7173	0.001927
0.3311	0.3028	0.003643
0.2954	0.5348	0.003049
0.7559	0.1144	0.007020
0.7332	0.2023	0.006308
0.2174	0.7125	0.002165
0.1327	0.5726	0.002046
0.4316	0.4963	0.003815
0.5311	0.4000	0.004590
0.2677	0.2487	0.003252
0.7456	0.1586	0.006637
0.5647	0.2682	0.005332
0.1538	0.2737	0.002415
0.1269	0.7392	0.001638
0.2913	0.1419	0.003510
0.1500	0.4790	0.002254
0.5006	0.1305	0.005255
0.5964	0.1223	0.006243

Table XVIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3824	0.4276	0.003572
0.1520	0.7702	0.001487
0.3239	0.3608	0.002991
0.2666	0.5766	0.002373
0.7407	0.1434	0.006409
0.7078	0.2375	0.005865
0.1971	0.7474	0.001725
0.1287	0.6383	0.001523
0.3874	0.5574	0.003102
0.4932	0.4514	0.003966
0.2277	0.2584	0.002334
0.7244	0.1926	0.006102
0.5445	0.3125	0.004755
0.1604	0.3299	0.001899
0.1079	0.7861	0.001257
0.2997	0.1747	0.002859
0.1319	0.5565	0.001628
0.5152	0.1585	0.004563
0.6016	0.1545	0.005330

Table XIX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.4410	0.3781	0.003696
0.1809	0.7261	0.001721
0.3419	0.3168	0.003151
0.3009	0.5439	0.002690
0.7612	0.1210	0.006849
0.7369	0.2019	0.006540
0.2264	0.7101	0.001991
0.1425	0.5908	0.001664
0.4354	0.4994	0.003591
0.5362	0.4014	0.004637
0.2397	0.2177	0.002407
0.7523	0.1578	0.006739
0.5753	0.2752	0.005168
0.1697	0.2876	0.001971
0.1310	0.7489	0.001438
0.3092	0.1515	0.002872
0.1539	0.5008	0.001788
0.5263	0.1385	0.004659
0.6128	0.1296	0.005635

Table XX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3958	0.3749	0.003924
0.1755	0.7208	0.001766
0.3299	0.3063	0.003605
0.2952	0.5319	0.002922
0.7658	0.1021	0.007224
0.7317	0.1986	0.006391
0.2285	0.7000	0.002135
0.1424	0.5685	0.002015
0.4323	0.4953	0.003699
0.5372	0.3914	0.004569
0.2280	0.2060	0.002913
0.7494	0.1508	0.006777
0.5642	0.2633	0.005162
0.1549	0.2741	0.002456
0.1214	0.7442	0.001536
0.2935	0.1365	0.003614
0.1460	0.4828	0.002226
0.5046	0.1277	0.005263
0.5973	0.1211	0.006181

Table XXI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Methyl-1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.4093	0.3787	0.003409
0.1800	0.7254	0.001444
0.3446	0.3136	0.002977
0.3053	0.5398	0.002401
0.7692	0.1149	0.006714
0.7352	0.2016	0.006135
0.2201	0.6960	0.001663
0.1583	0.5389	0.001514
0.4370	0.5014	0.003199
0.5390	0.3968	0.003952
0.2394	0.2206	0.002337
0.7509	0.1623	0.006201
0.5763	0.2733	0.004698
0.1731	0.2856	0.001893
0.1281	0.7457	0.001182
0.3013	0.1651	0.002702
0.1618	0.4950	0.001561
0.5260	0.1375	0.004388
0.6187	0.1247	0.005230

Table XXII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Methyl-1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.4012	0.3672	0.003745
0.1782	0.7163	0.001567
0.3714	0.2850	0.003805
0.3100	0.5193	0.002760
0.7631	0.1072	0.006943
0.7344	0.1962	0.006208
0.2270	0.7036	0.001791
0.1515	0.5619	0.001860
0.4411	0.4901	0.003459
0.5318	0.3966	0.004341
0.2283	0.2030	0.002919
0.7456	0.1544	0.006841
0.5612	0.2702	0.005041
0.1623	0.2702	0.002415
0.1308	0.7330	0.001310
0.2986	0.1420	0.003492
0.1437	0.4852	0.001971
0.5166	0.1284	0.005369
0.6000	0.1242	0.005988

Table XXIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3807	0.4253	0.003153
0.1570	0.7615	0.001304
0.3275	0.3555	0.002821
0.2711	0.5875	0.002297
0.7533	0.1324	0.006562
0.7084	0.2322	0.005881
0.1971	0.7463	0.001560
0.1357	0.6304	0.001403
0.3942	0.5466	0.003006
0.4988	0.4431	0.003806
0.2314	0.2491	0.002256
0.7291	0.1844	0.006114
0.5434	0.3132	0.004520
0.1595	0.3271	0.001824
0.1141	0.7783	0.001111
0.2960	0.1822	0.002706
0.1323	0.5525	0.001515
0.5120	0.1600	0.004478
0.5969	0.1526	0.005466

Table XXIV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2328	0.5360	0.001646
0.0818	0.8368	0.001120
0.1910	0.4336	0.001532
0.1558	0.6862	0.001442
0.6055	0.2124	0.002734
0.5445	0.3634	0.002633
0.1066	0.8334	0.001190
0.0678	0.6881	0.001171
0.2431	0.6884	0.001684
0.3233	0.6021	0.001959
0.1344	0.2940	0.001394
0.5682	0.2998	0.002688
0.3718	0.4350	0.002097
0.0892	0.3637	0.001273
0.0604	0.8286	0.001063
0.1741	0.2157	0.001491
0.0728	0.5952	0.001186
0.3429	0.2238	0.001936
0.4257	0.2215	0.002179

Table XXV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2513	0.4580	0.001993
0.0964	0.7913	0.001248
0.1983	0.3638	0.001895
0.1682	0.6280	0.001664
0.6137	0.1748	0.003024
0.5788	0.3198	0.002861
0.1250	0.7955	0.001330
0.0757	0.6158	0.001447
0.2762	0.6356	0.001916
0.3584	0.5467	0.002223
0.1297	0.2351	0.001796
0.5962	0.2489	0.002910
0.3900	0.3754	0.002425
0.0808	0.2986	0.001703
0.0656	0.7851	0.001209
0.1690	0.1717	0.001931
0.0802	0.5185	0.001556
0.3376	0.1781	0.002338
0.4234	0.1801	0.002544

Table XXVI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Butanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2276	0.4225	0.002015
0.0932	0.7567	0.001310
0.1718	0.3132	0.001956
0.1632	0.5790	0.001718
0.5686	0.1685	0.002936
0.5536	0.3029	0.002840
0.1237	0.7723	0.001370
0.0683	0.5553	0.001499
0.2684	0.6125	0.001967
0.3477	0.5235	0.002233
0.1032	0.1886	0.001889
0.5607	0.2398	0.002908
0.3549	0.3531	0.002347
0.0699	0.2412	0.001794
0.0642	0.7467	0.001244
0.1354	0.1357	0.001999
0.0721	0.4500	0.001604
0.2926	0.1472	0.002290
0.3690	0.1587	0.002408

Table XXVII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15 K

χ_B	χ_C	χ_A
0.2156	0.4883	0.001771
0.0883	0.8087	0.001042
0.1736	0.3808	0.001777
0.1508	0.6460	0.001441
0.5668	0.2090	0.002802
0.5307	0.3533	0.002694
0.1062	0.8154	0.001073
0.0582	0.6332	0.001247
0.2409	0.6702	0.001635
0.3160	0.5829	0.001957
0.1106	0.2440	0.001706
0.5496	0.2765	0.002789
0.3491	0.4060	0.002158
0.0728	0.3039	0.001604
0.0598	0.7858	0.001030
0.1475	0.1787	0.001796
0.0682	0.5334	0.001382
0.2989	0.1932	0.002128
0.3801	0.1870	0.002310

Table XXVIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2599	0.4757	0.001678
0.1216	0.7154	0.001187
0.2101	0.3818	0.001606
0.1797	0.6393	0.001403
0.6286	0.1793	0.002771
0.5848	0.3226	0.002707
0.1260	0.8067	0.001097
0.0783	0.6384	0.001124
0.2797	0.6428	0.001658
0.3701	0.5489	0.001989
0.1363	0.2517	0.001379
0.6043	0.2571	0.002765
0.4049	0.3828	0.002154
0.0936	0.3132	0.001305
0.0635	0.7636	0.000994
0.1801	0.1888	0.001505
0.0825	0.5438	0.001189
0.3591	0.1860	0.001937
0.4449	0.1868	0.002213

Table XXIX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2524	0.4595	0.001880
0.1268	0.7278	0.001278
0.1964	0.3626	0.001866
0.1781	0.6210	0.001542
0.6113	0.1772	0.002909
0.5762	0.3165	0.002762
0.1269	0.7901	0.001171
0.0746	0.6175	0.001308
0.2759	0.6369	0.001726
0.3640	0.5399	0.002047
0.1280	0.2295	0.001772
0.5913	0.2523	0.002858
0.3941	0.3715	0.002319
0.0826	0.2921	0.001659
0.0652	0.7881	0.001060
0.1714	0.1637	0.001892
0.0784	0.5205	0.001460
0.3387	0.1759	0.002233
0.4265	0.1711	0.002420

Table XXX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2275	0.5065	0.001686
0.0843	0.8172	0.000873
0.1837	0.4095	0.001705
0.1528	0.6687	0.001280
0.5867	0.2124	0.002844
0.5445	0.3604	0.002651
0.1119	0.8176	0.000927
0.0664	0.6514	0.001119
0.2460	0.6726	0.001467
0.3283	0.5865	0.001801
0.1244	0.2662	0.001679
0.5708	0.2795	0.002763
0.3601	0.4187	0.002126
0.0802	0.3299	0.001554
0.0585	0.8147	0.000829
0.1689	0.1899	0.001821
0.0735	0.5603	0.001256
0.3320	0.1972	0.002228
0.4149	0.2018	0.002380

Table XXXI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2048	0.4725	0.001883
0.0829	0.7919	0.001078
0.1571	0.3599	0.001868
0.1444	0.6322	0.001477
0.5557	0.1911	0.002866
0.5146	0.3534	0.002707
0.1064	0.8015	0.001114
0.0611	0.6006	0.001285
0.2761	0.6272	0.001783
0.3104	0.5792	0.002007
0.1013	0.2196	0.001817
0.5267	0.2862	0.002812
0.3307	0.4042	0.002260
0.0673	0.2755	0.001700
0.0581	0.7822	0.001021
0.1353	0.1581	0.001946
0.0636	0.5051	0.001432
0.2819	0.1716	0.002258
0.3502	0.1940	0.002409

Table XXXII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Methyl-1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2279	0.4132	0.001816
0.0943	0.7510	0.000991
0.1766	0.3052	0.001848
0.1634	0.5744	0.001414
0.5694	0.1686	0.002811
0.5573	0.3059	0.002740
0.1268	0.7694	0.001032
0.0697	0.5503	0.001229
0.2681	0.6128	0.001594
0.3527	0.5251	0.001946
0.1058	0.1875	0.001818
0.5620	0.2305	0.002810
0.3639	0.3433	0.002222
0.0740	0.2402	0.001653
0.0696	0.7413	0.000939
0.1400	0.1377	0.001941
0.0703	0.4527	0.001375
0.2902	0.1523	0.002268
0.3756	0.1556	0.002402

Table XXXIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Methyl-1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2541	0.4532	0.001815
0.0958	0.7912	0.000968
0.1957	0.3630	0.001784
0.1773	0.6224	0.001382
0.6149	0.1748	0.002910
0.5803	0.3132	0.002725
0.1278	0.7938	0.001026
0.0753	0.6137	0.001175
0.2807	0.6333	0.001616
0.3619	0.5407	0.002003
0.1286	0.2319	0.001752
0.5963	0.2453	0.002832
0.3924	0.3733	0.002213
0.0833	0.2919	0.001562
0.0679	0.7838	0.000917
0.1731	0.1666	0.001888
0.0798	0.5198	0.001310
0.3384	0.1793	0.002223
0.4235	0.1839	0.002461

Table XXXIV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2336	0.1486	0.001486
0.0834	0.8265	0.000808
0.1926	0.4284	0.001416
0.1589	0.6771	0.001143
0.5998	0.2146	0.002666
0.5476	0.3587	0.002542
0.1471	0.7714	0.001030
0.0684	0.6779	0.000905
0.2492	0.6802	0.001431
0.3314	0.5913	0.001763
0.1293	0.2886	0.001319
0.5654	0.2981	0.002577
0.3732	0.4279	0.001915
0.0885	0.3575	0.117300
0.0585	0.8278	0.000742
0.1770	0.2093	0.001424
0.0747	0.5888	0.001014
0.3485	0.2137	0.001865
0.4303	0.2133	0.002153

Table XXXV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2085	0.4629	0.001764
0.0804	0.7946	0.000901
0.1595	0.3583	0.001829
0.1423	0.6291	0.001337
0.5532	0.1930	0.002866
0.5205	0.3386	0.002609
0.1095	0.8006	0.000943
0.0624	0.5968	0.001176
0.2398	0.6594	0.001487
0.3150	0.5723	0.001816
0.0876	0.2459	0.001783
0.5322	0.2793	0.002725
0.3408	0.3834	0.002166
0.0659	0.2768	0.001631
0.0581	0.7789	0.000876
0.1342	0.1578	0.001903
0.0649	0.5031	0.001330
0.2799	0.1784	0.002287
0.3611	0.1831	0.002434

Table XXX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2275	0.5065	0.001686
0.0843	0.8172	0.000873
0.1837	0.4095	0.001705
0.1528	0.6687	0.001280
0.5867	0.2124	0.002844
0.5445	0.3604	0.002651
0.1119	0.8176	0.000927
0.0664	0.6514	0.001119
0.2460	0.6726	0.001467
0.3283	0.5865	0.001801
0.1244	0.2662	0.001679
0.5708	0.2795	0.002763
0.3601	0.4187	0.002126
0.0802	0.3299	0.001554
0.0585	0.8147	0.000829
0.1689	0.1899	0.001821
0.0735	0.5603	0.001256
0.3320	0.1972	0.002228
0.4149	0.2018	0.002380

Table XXXVII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 2-Methyl-1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2585	0.4763	0.001585
0.0982	0.7999	0.000878
0.2043	0.3769	0.001471
0.1784	0.6378	0.001246
0.6270	0.1809	0.002734
0.5870	0.3217	0.002615
0.1664	0.7408	0.001907
0.0766	0.6373	0.000980
0.2818	0.6390	0.001529
0.3696	0.5440	0.001871
0.1332	0.2526	0.001348
0.6055	0.2554	0.002708
0.4056	0.3856	0.002051
0.0922	0.3174	0.001217
0.0646	0.8027	0.000798
0.1823	0.1789	0.001462
0.0775	0.5460	0.001056
0.3585	0.1807	0.001916
0.4490	0.1806	0.002187

Table XXXVIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Dibutyl Ether (B), 1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2322	0.5275	0.001614
0.0841	0.8301	0.000976
0.1911	0.4260	0.001530
0.1564	0.6849	0.001292
0.6297	0.2036	0.002825
0.5363	0.3822	0.002608
0.0954	0.8520	0.000987
0.0671	0.6827	0.001028
0.2596	0.6760	0.001633
0.3345	0.6094	0.001956
0.1563	0.3499	0.001432
0.5910	0.2741	0.002829
0.3955	0.4020	0.002143
0.0880	0.3581	0.001265
0.0546	0.8429	0.000866
0.1782	0.1955	0.001538
0.0736	0.5961	0.001128
0.3493	0.2152	0.001955
0.4710	0.1778	0.002308

Table XXXIX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3022	0.4800	0.001600
0.1115	0.8065	0.000979
0.2499	0.4044	0.001488
0.2072	0.6457	0.001276
0.6787	0.1790	0.002437
0.6282	0.2999	0.002348
0.1462	0.7985	0.001023
0.0925	0.6599	0.001038
0.3160	0.6206	0.001537
0.4845	0.4368	0.001987
0.1683	0.2757	0.001360
0.6553	0.2404	0.002409
0.4532	0.3780	0.001930
0.1153	0.3511	0.001242
0.0777	0.8149	0.000890
0.2289	0.2005	0.001464
0.0987	0.5773	0.001102
0.4327	0.1895	0.001839
0.5133	0.1858	0.002064

Table XL

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2947	0.4682	0.001808
0.1100	0.7996	0.001041
0.2370	0.3877	0.001772
0.2008	0.6364	0.001430
0.6685	0.1665	0.002606
0.6234	0.2953	0.002445
0.1479	0.7864	0.001099
0.0972	0.6397	0.001274
0.3048	0.6218	0.001584
0.4049	0.5218	0.001860
0.1617	0.2541	0.001747
0.6442	0.2377	0.002504
0.4380	0.3753	0.002112
0.1122	0.3485	0.001620
0.0817	0.8003	0.001007
0.2252	0.1761	0.001906
0.1045	0.5491	0.001400
0.4171	0.1774	0.002241
0.5027	0.1723	0.002364

Table XLI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3609	0.3797	0.002108
0.1106	0.7642	0.001097
0.2156	0.3313	0.001919
0.1861	0.5961	0.001505
0.6372	0.1605	0.002763
0.6054	0.2827	0.002527
0.1427	0.7713	0.001139
0.0837	0.5888	0.001309
0.3018	0.5987	0.001640
0.3884	0.5038	0.001926
0.1254	0.2070	0.001847
0.4682	0.2435	0.002454
0.4188	0.3410	0.002234
0.0928	0.2731	0.001711
0.0766	0.7673	0.001040
0.1829	0.1550	0.002009
0.0858	0.4915	0.001458
0.3584	0.1570	0.002355
0.4554	0.1701	0.002509

Table XLII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Butanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2924	0.3834	0.002029
0.1261	0.7353	0.001317
0.2219	0.2995	0.002012
0.2108	0.5456	0.001703
0.6489	0.1337	0.002751
0.6380	0.2493	0.002632
0.1627	0.7392	0.001372
0.0926	0.5374	0.001513
0.3406	0.5590	0.001892
0.4386	0.4583	0.002157
0.1302	0.1867	0.001887
0.6408	0.1929	0.002721
0.4470	0.3027	0.002385
0.0951	0.2279	0.001804
0.0838	0.7343	0.001240
0.1815	0.1329	0.002011
0.0941	0.4406	0.001613
0.3650	0.1327	0.002401
0.4531	0.1367	0.002578

Table XLIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3186	0.4215	0.001951
0.1244	0.7650	0.001290
0.2514	0.3428	0.001888
0.2343	0.6079	0.001646
0.6864	0.1531	0.002672
0.6494	0.2620	0.002589
0.1646	0.7591	0.001334
0.1017	0.6011	0.001444
0.3504	0.5685	0.001888
0.4497	0.4698	0.002124
0.1650	0.2237	0.001808
0.6740	0.1968	0.002660
0.4775	0.3220	0.002315
0.1085	0.2898	0.001703
0.0924	0.7674	0.001247
0.2210	0.1638	0.001908
0.1105	0.5035	0.001555
0.4260	0.1563	0.002281
0.5097	0.1507	0.002406

Table XLIV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 1-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3297	0.4312	0.001732
0.1350	0.7684	0.001194
0.2702	0.3551	0.001591
0.2799	0.5637	0.001543
0.7041	0.1461	0.002518
0.6701	0.2538	0.002571
0.1717	0.7595	0.001302
0.1023	0.6194	0.001223
0.3537	0.5745	0.001791
0.4492	0.4738	0.002040
0.1847	0.2425	0.001402
0.6817	0.2069	0.002490
0.4894	0.3289	0.001993
0.1286	0.3028	0.001332
0.0935	0.7783	0.001105
0.2380	0.1708	0.001473
0.1111	0.5273	0.001279
0.4425	0.1612	0.001862
0.5261	0.1594	0.002062

Table XLV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Butanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2945	0.3777	0.002005
0.1268	0.7317	0.001145
0.2292	0.2879	0.002021
0.2184	0.5452	0.001632
0.6551	0.1352	0.002762
0.6462	0.2438	0.002619
0.1666	0.7336	0.001192
0.0909	0.5448	0.001403
0.3364	0.5587	0.001730
0.4409	0.4484	0.002060
0.1417	0.1748	0.001923
0.6446	0.1956	0.002631
0.4488	0.2987	0.002332
0.0917	0.2284	0.001802
0.0853	0.7320	0.001076
0.1655	0.1368	0.002016
0.0957	0.4342	0.001567
0.3628	0.1365	0.002403
0.4469	0.1467	0.002520

Table XLVI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Butanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3189	0.4228	0.001853
0.1326	0.7613	0.001104
0.2637	0.3344	0.001880
0.2319	0.5806	0.001501
0.6940	0.1418	0.002665
0.6557	0.2575	0.002529
0.1704	0.7523	0.001165
0.1045	0.5936	0.001297
0.3546	0.5662	0.001691
0.4394	0.4763	0.001935
0.1649	0.2250	0.001796
0.6730	0.1997	0.002615
0.4787	0.3215	0.002221
0.1207	0.2804	0.001659
0.0938	0.7647	0.001041
0.2274	0.1576	0.001992
0.1113	0.5096	0.001425
0.4222	0.1570	0.002224
0.5136	0.1474	0.002376

Table XLVII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Butanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3282	0.4312	0.001618
0.1349	0.7721	0.001025
0.2709	0.3482	0.001528
0.2341	0.5960	0.001357
0.7080	0.1379	0.002437
0.6683	0.2531	0.002394
0.1919	0.7358	0.001168
0.1111	0.6038	0.001114
0.3550	0.5714	0.001662
0.4500	0.4744	0.001924
0.1751	0.2358	0.001377
0.6829	0.2037	0.002384
0.4879	0.3308	0.001945
0.1069	0.3059	0.001267
0.0923	0.7822	0.000947
0.4887	0.1040	0.001881
0.1066	0.5314	0.001150
0.4415	0.1627	0.001854
0.5336	0.1569	0.002052

Table XLVIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Methyl-1-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2866	0.3853	0.001806
0.1285	0.7310	0.000984
0.2268	0.2948	0.001863
0.2201	0.5440	0.001429
0.6512	0.1402	0.002672
0.4803	0.4359	0.001960
0.1668	0.7338	0.001030
0.0977	0.5295	0.001265
0.3440	0.5467	0.001575
0.4361	0.4523	0.001871
0.1388	0.1798	0.001824
0.6134	0.1835	0.002560
0.4470	0.3010	0.002166
0.1026	0.2305	0.001714
0.0936	0.7256	0.000944
0.1453	0.1375	0.001868
0.0978	0.4371	0.001426
0.3661	0.1325	0.002275
0.3237	0.4255	0.001786

Table XLIX

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Methyl-1-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3156	0.4155	0.001739
0.1463	0.7468	0.000997
0.2614	0.3293	0.001782
0.2333	0.5789	0.001371
0.6904	0.1447	0.002521
0.6657	0.2504	0.002359
0.1724	0.7503	0.099400
0.1072	0.5909	0.001205
0.3531	0.5647	0.001549
0.4487	0.4690	0.001813
0.1707	0.2189	0.001758
0.6803	0.2013	0.002431
0.4752	0.3194	0.002069
0.1239	0.2790	0.001604
0.0943	0.7631	0.000910
0.2230	0.1799	0.001854
0.1141	0.4995	0.001348
0.4188	0.1582	0.002172
0.5096	0.1539	0.002273

Table L

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl tert-Butyl Ether (B), 2-Methyl-1-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3310	0.4287	0.001505
0.1367	0.7633	0.000877
0.2781	0.3455	0.001451
0.2387	0.5900	0.001200
0.7001	0.1460	0.002284
0.6674	0.2535	0.002302
0.1780	0.7542	0.000946
0.1080	0.6133	0.001005
0.3615	0.5652	0.001457
0.4562	0.4708	0.001699
0.1858	0.2349	0.001328
0.6859	0.1989	0.002328
0.4993	0.3194	0.001877
0.1303	0.3031	0.001207
0.0957	0.7748	0.000819
0.2420	0.1668	0.001422
0.1158	0.5180	0.001068
0.4469	0.1594	0.001794
0.5327	0.1546	0.001963

Table LI

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Propanol (C), and 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3025	0.4726	0.001460
0.1206	0.7908	0.000804
0.2525	0.3923	0.001376
0.2070	0.6393	0.001109
0.6818	0.1686	0.002368
0.6307	0.2938	0.002241
0.1496	0.7893	0.000834
0.0976	0.6857	0.000913
0.3152	0.6239	0.001342
0.4167	0.5169	0.001631
0.1770	0.2681	0.001322
0.6584	0.2294	0.002338
0.4583	0.3673	0.001810
0.1127	0.3450	0.001165
0.0794	0.8074	0.000724
0.2333	0.1945	0.001405
0.1051	0.5692	0.001011
0.4251	0.1994	0.001806
0.5172	0.1817	0.001986

Table LII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Propanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2684	0.4257	0.001814
0.1104	0.7651	0.000908
0.2071	0.3401	0.001828
0.1942	0.5880	0.001358
0.6292	0.1609	0.002702
0.6041	0.2785	0.002452
0.1476	0.7665	0.000933
0.0837	0.5791	0.001213
0.3053	0.5976	0.001485
0.3940	0.5050	0.001732
0.1359	0.2086	0.001894
0.6158	0.2294	0.002543
0.4239	0.3334	0.002145
0.0917	0.2700	0.001695
0.0785	0.7589	0.000878
0.1798	0.1527	0.002003
0.0907	0.4852	0.001384
0.3556	0.1580	0.002374
0.4460	0.1585	0.002497

Table LIII

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Propanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.2981	0.4593	0.001647
0.1152	0.7896	0.000851
0.2456	0.3720	0.001677
0.2049	0.6272	0.001235
0.6691	0.1703	0.002549
0.6300	0.2941	0.002436
0.1504	0.7829	0.000893
0.0924	0.6382	0.001106
0.3091	0.6181	0.001385
0.4051	0.5175	0.001670
0.1605	0.2579	0.001648
0.6447	0.2380	0.002438
0.4527	0.3594	0.001997
0.1123	0.3186	0.001529
0.0848	0.7918	0.082800
0.2166	0.1846	0.001818
0.0969	0.5478	0.001254
0.4052	0.1804	0.002107
0.4890	0.1818	0.002256

Table LIV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary 1,4-Dioxane (B), 2-Pentanol (C), and Heptane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.4330	0.3280	0.004460
0.2364	0.1829	0.003178
0.2039	0.6823	0.002265
0.7705	0.1756	0.006974
0.3425	0.2770	0.003887
0.5900	0.2381	0.005727
0.3247	0.4946	0.003355
0.1681	0.2343	0.002629
0.7686	0.0977	0.002906
0.1456	0.7045	0.001928
0.7518	0.1764	0.006786
0.2910	0.1317	0.003668
0.2535	0.6732	0.002505
0.1569	0.4410	0.002371
0.1533	0.5284	0.002287
0.5111	0.1278	0.005471
0.4689	0.4531	0.004175
0.6015	0.1178	0.006068
0.5679	0.3567	0.005029

Table LV

Experimental Mole Fraction Solubilities Of Anthracene (χ_A) in Ternary Methyl *tert* -Butyl Ether (B), 2-Pentanol (C), and Cyclohexane (D) Solvent Mixtures at 298.15K

χ_B	χ_C	χ_A
0.3127	0.3460	0.002107
0.1389	0.1583	0.001942
0.1443	0.6950	0.001388
0.6760	0.1554	0.002627
0.2356	0.2596	0.002067
0.3745	0.4052	0.002126
0.2370	0.5022	0.001793
0.0997	0.2014	0.001833
0.6625	0.1223	0.002738
0.0972	0.6962	0.001322
0.6767	0.2150	0.002641
0.1822	0.1116	0.002085
0.1808	0.7072	0.001444
0.0980	0.4029	0.001712
0.1039	0.4961	0.001615
0.3807	0.1185	0.002467
0.3700	0.5120	0.001985
0.4642	0.1199	0.002610
0.4649	0.4212	0.002181

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